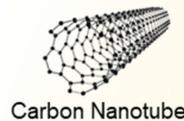


Recent Progress in Stretchable Batteries for Wearable Electronics

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Stretchable batteries

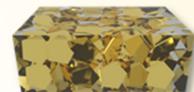
Material designs



Carbon Nanotube

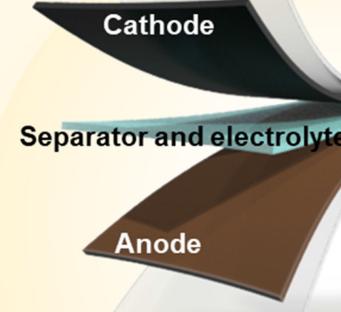


Metal Nanosheet



Hybrid polymer composite

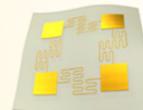
Packaging materials



Structure designs



Wavy/buckled

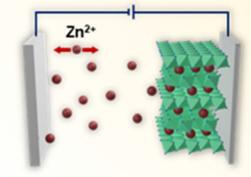


Island-Bridge

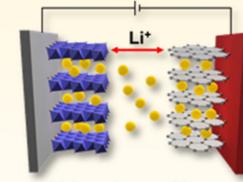


Origami/Kirigami

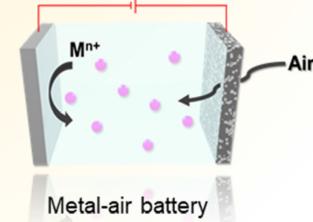
Battery systems



Mvalent-based battery



Lithium-based battery



Metal-air battery

With the rapidly approaching implementation of wearable electronic devices such as implantable devices, stretchable sensors, and healthcare devices, stretchable power sources have aroused worldwide attention as a key component in this emerging field. Among stretchable power sources, batteries, which store electrical energy through redox reactions during charge/discharge processes, are an attractive candidate because of their high energy density, high output voltage, and long-term stability. In recent years, extensive efforts have been devoted to developing new materials and innovative structural designs for stretchable batteries. This review covers the latest advances in stretchable batteries, focusing on advanced stretchable materials and their design strategies. First, we provide a detailed

overview of the materials aspects of components in a stretchable battery, including electrode materials, solid-state electrolytes, and stretchable separator membranes. Second, we provide an overview on various structural engineering strategies to impart stretchability to batteries (i.e., wavy/buckling structures, island-bridge structures, and origami/kirigami structures). Third, we summarize recently reported developments in stretchable batteries based on various chemistries, including Li-based batteries, multivalent-based batteries, and metal-air batteries. Finally, we discuss the future perspectives and remaining challenges toward the practical application of stretchable batteries with reliable mechanical robustness and stable electrochemical performance under a physical strain.

1. Introduction

Recently, wearable electronic devices with new features such as stretchability have been attracting substantial interest in both industry and academia because of their potential applications in, for example, implantable devices,^[1] healthcare devices,^[2] artificial skin,^[3] and soft robotics with arbitrarily shaped surfaces.^[4] However, traditional electronic systems based on rigid and fragile silicon semiconductors are not applicable to such devices.^[5] For the practical realization of highly reliable wearable electronics, their components, including transistors,^[6] circuit boards,^[7] integrated wires,^[8] and power supplies,^[9] should be stretchable while maintaining their functionality. Indeed, extensive effort has been devoted to exploiting new materials and innovative structural designs to realize wearable devices that can accommodate mechanical strain. This effort has led to the development of stretchable semiconductors and stretchable electrode that demonstrate high performance under extreme deformations. By comparison, the progress in stretchable energy-storage devices (e.g., supercapacitor and batteries) that power wearable devices have lagged. Hence, stretchable energy-storage devices are attracting increasing research attention and remain a great challenge for the realization of wearable electronic devices.^[10]

One of the candidate energy-storage devices for use in stretchable power supplies is a supercapacitor, which provides special features such as fast charge/discharge, high power density, and good long-term cyclability.^[11] As a result, proof-of-concept stretchable supercapacitors based on various strategies have been developed.^[12] Despite tremendous promising results, supercapacitors are not a suitable energy-storage system for practical applications in wearable devices because of their low energy density and inadequate working voltage.^[13] Compared with supercapacitors, batteries, which store electricity through redox relations, have been widely recognized as an ideal stretchable energy-storage system because of their advantages, which include the lack of a memory effect, high energy density, high working voltage, and good long-term stability.^[14] Furthermore, batteries have already been used to power various consumer devices such as portable electronics and personal electronics.^[15] A series of excellent reviews have already covered stretchable supercapacitors very well; this review is therefore mainly focused on stretchable batteries.^[16]

The history of the development of stretchable batteries is illustrated in Figure 1. Firstly, Whiteside and coworkers demonstrated stretchable electronics comprising single crystal silicon on the elastic substrate.^[17] After introducing the stretchable concept, many researchers have widely studied a variety of methods to develop stretchable batteries as a power source for wearable electronics. Firstly, stretchable primary Zn-based batteries ($Zn-MnO_2$ ^[18a] and $Zn-Ag$ ^[18b]) based on coplanar structure were reported. They successfully delivered power to the device even under strain, but was not rechargeable. Since 2013, in order to meet the demands of wearable devices such as the long-term life and wide operating voltage window, Li-ion batteries (LIBs) which are a representative rechargeable battery system have been proposed as a stretchable power source using various strategies.^[18c-g] These prototypes, however, presented limitations in terms of energy density. To overcome the above issues, a three-dimensional (3D) porous electrode structures^[18h] or high energy battery systems (e.g., metal-air^[18i] and multivalent batteries^[18j]) were introduced to realize stretchable rechargeable batteries.^[18k-l] Recently, the safety issue of stretchable batteries as a power supplier for wearable devices has attracted significant research interests. Hence, stretchable

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batteries based on an aqueous electrolyte such as aqueous Li-ion batteries (ARBs)^[18m] and aqueous Zn-MnO₂ batteries^[18n] have been reported. Furthermore, stretchable Li-metal batteries with high energy density have been demonstrated.^[18o]

In this review, we cover two strategies toward developing reliable stretchable batteries: the use of recently advanced materials (e.g., carbon nanotubes, graphene, metal nanowires, and conducting materials) and promising structural design (e.g., wavy/buckling, island-bridge, and origami/kirigami structures). In addition, we summarize the recent developments reported for state-of-the-art stretchable batteries (e.g., Li-based batteries, multivalent-based batteries, and metal-air batteries). At the end of this review, we discuss the future perspectives and remaining challenges toward the practical application of stretchable batteries with reliable mechanical robustness and stable electrochemical performance under physical deformations.

2. Materials for Stretchable Batteries

In general, batteries, which are composed of hard and brittle components such as electrodes, separator membranes, and packaging materials, do not satisfy the requirements for wearable devices because their functions cannot withstand strain.^[19] Researchers have devoted extensive effort to imparting battery components with stretchability and to designing innovative structures to realize stretchable batteries for reliable wearable devices.

2.1. Electrode Materials

Among the components of batteries, the electrode is a key element for constructing stretchable batteries. Normally, an

electrode slurry is fabricated by mixing active materials, polymeric binders (e.g., polyvinylidene fluoride (PVDF)), and conducting agents (e.g., Super P carbon black) and subsequently coated onto the surface of a metal current collector (e.g., copper or aluminum), which should have high electrical conductivity to promote electron transfer between the active materials and an external wire.^[20] When physical strain is applied to the electrode consisted of rigid materials, they do not withstand delamination of the electrode slurry materials from the current collector, resulting in severe degradation of the battery performance. Furthermore, metal-based current collectors exhibit low stretchability (strain less than 2%).^[21] One of the most important factors of the stretchable current collector is how to design stable electrical performance during deformations. This is because it is closely related to the battery performance. To overcome these issues, investigators have attempted to design stretchable materials and stretchable current collectors by using a variety of methods.^[22] In this section, we will survey recent progress in the development of new materials for stretchable electrodes, including carbon-based materials, metal-based materials, hybrid nanocomposite materials, and conducting polymer.

2.1.1. Carbon-Based Materials

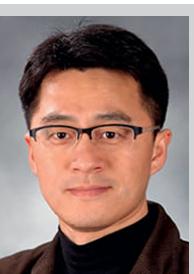
Because of their unique features, which include high electrical conductivity, excellent mechanical, and chemical stability,^[23] carbon-based materials such as carbon nanotubes (CNTs), graphite, and graphene are considered as one of the most promising materials for stretchable electrodes.^[24] Among them, CNTs exhibit an inherently high aspect ratio, superior electrical conductivity, high surface area, porous network, and mechanical robustness, making them attractive as an active material and current collector for stretchable batteries.^[25] The CNTs with



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Seungmin Yoo received his M.S in Material Science and Engineering at POSTECH in 2004. He entered LG Chemical R&D and developed polymeric binders and films from 2004 to 2011. And then he received Ph.D. in School of Energy and Chemical Engineering at UNIST. Now he has joined in chemical engineering at Ulsan College as an assistant professor from 2015. He has been studying polymer-based materials in energy conversion and storage devices.



Unyong Jeong received his Ph.D. in Chemical Engineering from POSTECH in Korea. After he spent two years as a postdoctoral research associate at University of Washington, he joined to Yonsei University in 2006, and he moved to Materials Science and Engineering at POSTECH. His research interest includes organic/inorganic hybrid materials for electronic devices, synthesis of nanostructured materials, and assembly of nano- and micro-structured materials.



Soojin Park received his Ph.D. in Chemistry from POSTECH in Korea. After he spent three years as a postdoctoral research associate at University of Massachusetts at Amherst, he joined to UNIST in 2009, and he moved to Chemistry department at POSTECH. His research interest includes design of deformable batteries, synthesis of high capacity organic/inorganic anode materials, synthesis of polymeric binder and separator for rechargeable batteries.

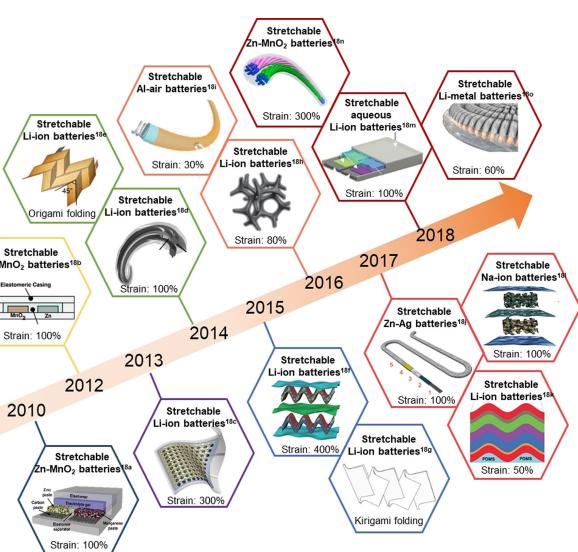


Figure 1. A chronology of the development of state-of-the-art stretchable batteries. Images reproduced with permission as follows: “Stretchable Zn-MnO₂ batteries with coplanar configuration.” Reproduced with permission.^[18a] Copyright 2010, Wiley-VCH. “Stretchable Zn-MnO₂ batteries based on fabric substrate.” Reproduced with permission.^[18b] Copyright 2012, Wiley-VCH. “Stretchable LIBs based on serpentine configuration.” Reproduced with permission.^[18c] Copyright 2013, Macmillan Publishers Limited. “Fiber-shaped stretchable LIBs.” Reproduced with permission.^[18d] Copyright 2014, Wiley-VCH. “Origami batteries.” Reproduced with permission.^[18e] Copyright 2014, Macmillan Publishers Limited. “Stretchable LIBs based on buckling configuration.” Reproduced with permission.^[18f] Copyright 2015, Wiley-VCH. “Kirigami batteries.” Reproduced with permission.^[18g] Copyright 2015, Macmillan Publishers Limited. “Stretchable LIBs based on Si/C composite.” Reproduced with permission.^[18h] Copyright 2016, Wiley-VCH. “Fiber-shaped stretchable Al-air batteries.” Reproduced with permission.^[18i] Copyright 2016, Wiley-VCH. “Stretchable Zn–Ag batteries based on serpentine layout.” Reproduced with permission.^[18j] Copyright 2017, American Association for the Advancement of Science. “Stretchable wavy LIBs.” Reproduced with permission.^[18k] Copyright 2017, Wiley-VCH. “Stretchable Na-ion batteries.” Reproduced with permission.^[18l] Copyright 2017, Wiley-VCH. “Stretchable aqueous LIBs.” Reproduced with permission.^[18m] Copyright 2018, Wiley-VCH. “Fiber-shaped stretchable Zn-MnO₂ batteries” Reproduced with permission.^[18n] Copyright 2018, American Chemical Society. “Stretchable Li metal batteries.” Reproduced with permission.^[18o] Copyright 2018, Elsevier.

one-dimensional features enable the effective construction of an electrically interconnected percolation network, which helps maintain the electrical conduction pathway under strain.^[26] Moreover, CNTs can be easily fabricated as a stretchable current collector on stretchable substrates using spray-coating, spin-coating, vacuum filtration, and printing methods.^[27] An aligned CNT array can also be used in the fabrication of stretchable current collectors because of its unique mechanical properties and excellent electrical conductivity. Peng and coworkers developed freestanding CNT fiber spring that could serve as a highly stretchable current collector and substrate for stretchable LIBs.^[28] Figure 2a and b shows that the spring-like fiber was designed by twisting several CNT fibers with a diameter of approximately 12 µm and a high electrical conductivity of 10^2 – 10^3 S cm⁻¹ along the fiber axis, which can facilitate a high level of strain (300% uniaxial strain). The scanning electron microscopy (SEM) images in Figure 2c, show that the CNTs are highly aligned along the helical direction. The morphologies of the spring-like CNT fibers under stretching/releasing conditions

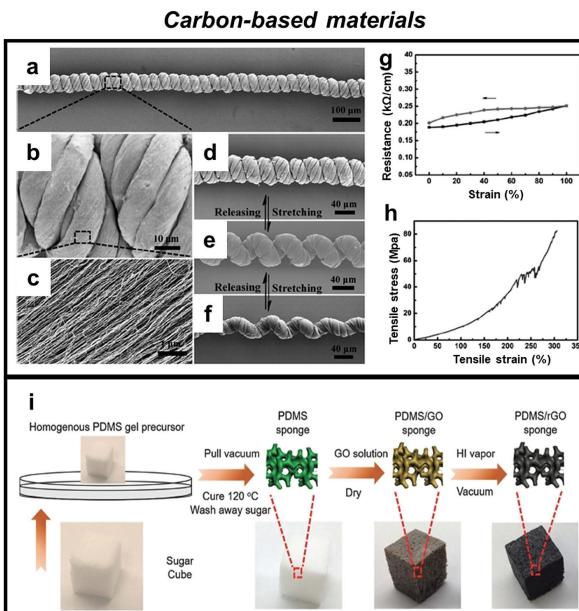


Figure 2. Carbon-based materials for stretchable batteries. a)–c) Scanning electron microscopy (SEM) images of a spring-like fiber at different magnifications. d)–f) SEM images of a fiber at different strains: 0% (d) 50% (e), and 100% (f). g) Evolution of resistances of the fiber during a stretch and release process with a strain of 100%. h) Tensile stress-strain curve of a fiber. Reproduced with permission. Copyright 2014, Wiley-VCH.^[28] i) Schematic of preparation steps of a conductive PDMS/rGO sponge. The PDMS/GO sponge (insulating) was brownish in color; after the material was reduced to rGO (conductive), it appeared black. Reproduced with permission. Copyright 2017, Wiley-VCH.^[18i]

were observed by SEM, which demonstrate that they could maintain their initial structure without sustaining any damage (Figure 2d–f). Also, the electrical resistance of the spring-like CNT fibers did not substantially change after stretching/releasing at a strain of 100% (Figure 2g and h). To achieve stretchable fiber-shaped LIBs, active materials ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and LiMn_2O_4 (LMO)) were incorporated into the as-prepared CNT fibers to fabricate stretchable electrodes; the stretchable fiber batteries were then assembled with the stretchable electrodes and a gel electrolyte that served as both an electrolyte and a separator membrane. Peng et al. also demonstrated freestanding aligned CNT sheets as a current collector and a cathode for stretchable fiber-shaped Zn-air batteries. Air permeability is one of the most important factors affecting the air electrode of a metal-air battery.^[29] The prepared CNT electrode structure greatly facilitated air diffusion from the atmosphere to the active sites. To this end, the arrangement and number of stacked CNT sheets were precisely controlled, resulting in a successful demonstration of stretchable Zn-air batteries.

Graphene has been widely used in the stretchable electronics field because of its outstanding properties such as excellent electrical conductivity and high mechanical robustness.^[30] Yu and coworkers designed a stretchable current collector by using 3D porous poly(dimethylsiloxane) (PDMS) sponge and reduced graphene oxide (rGO) as an elastic supporter and a conducting agent, respectively (Figure 2i).^[18i]

The PDMS sponge with an open network of pores (an average volume of 2.74 cm^3 and porosity of ~6.7%) was typically fabricated using a cost-effective sugar template. The PDMS sponge was then immersed in a graphene oxide (GO) solution (5 mg mL^{-1}). A reduction process was subsequently carried out using hydrogen iodide (HI) vapor as a reducing agent to change GO into rGO because rGO exhibits greater electrical conductivity than GO. The prepared PDMS/rGO sponges served as a stretchable current collector with high stretchability and high electrical conductivity. Using the PDMS/rGO sponge, the authors developed a stretchable Na-ion battery that could supply power to a light-emitting diode (LED) device stably even at a strain of 50%.

2.1.2. Metal-Based Materials

Metal-based materials, such as silver, gold, lithium, and copper, can be used as a stretchable current collector and/or an active material in batteries.^[31] Compared with carbon-based materials, metal-based materials typically have higher electrical conductivity (10^7 S m^{-1} at 20°C), which enables electrons to be effectively transferred to them as active materials, resulting in an increase in the charge/discharge rate.^[32] For this reason, metal-based materials (e.g., copper, aluminum, and stainless steel) have typically been used as current collectors. Three-dimensional stainless steel mesh as a current collector for flexible energy-storage devices was proposed. This structure of current collector guaranteed high energy density and outstanding rate performance due to its smaller thickness and high electrical conductivity.^[33] Furthermore, Tong et al. proposed three-dimensional nickel nitride (Ni_3N) nanosheets grown on a 3D carbon substrate as a free-standing electrode for flexible LIBs. The cell based on the Ni_3N electrode exhibited an excellent battery performance and reasonable flexibility.^[34] However, because metal-based materials exhibit intrinsically low stretchability (< 2% strain), they cannot be directly used in stretchable batteries. Various approaches have been adopted to impart stretchability to bulk metal-based materials *via* structural engineering (e.g., serpentine layouts and buckled structures).^[35] For example, Wallace et al. prepared a stretchable current collector that was fabricated by simple deposition of Au metal onto a pre-strained poly(styrene-*b*-isoprene-*b*-butadiene-*b*-styrene) (SIBS) elastomer substrate, as shown in Figure 3a and b.^[36] This wavy structural electrode maintained electrical conductivity at 30% strain even after 2000 stretching cycles (Figure 3c). Steingart and coworkers demonstrated a stretchable silver-coated fabric for stretchable Zn-MnO₂ batteries (Figure 3d and e), which could be stretched up to 100% without any sacrificing electrochemical performance (Figure 3f).^[18b]

Recently, Li-metal batteries have received extensive interest in the battery research community because of their strong performance, highlighted by a high theoretical capacity (3860 mAh g^{-1}) and low electrochemical potential (-3.040 V versus standard hydrogen electrode, SHE).^[37] Very recently, Cui et al. proposed the first stretchable Li metal anode that can maintain its electrochemical performance under physical strain,

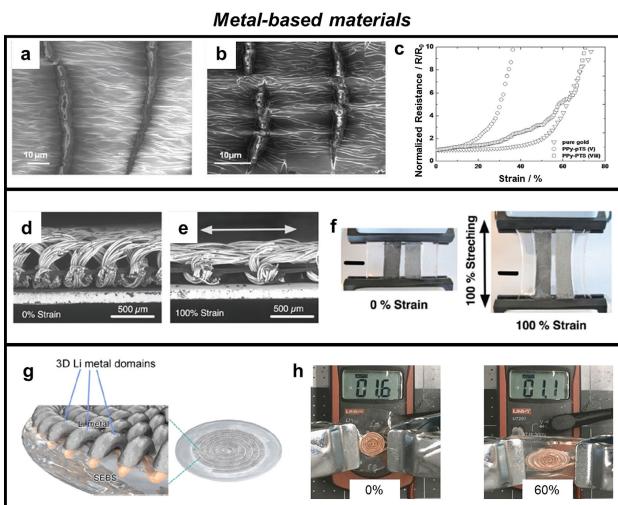


Figure 3. Carbon-based materials for stretchable batteries. Field-emission SEM images: a) buckled Au film; b) buckled PPy-pTS (polypyrrole (PPy)-*p*-toluenesulfonate anion (*p*TS)) film. c) Normalized electrical resistances versus tensile strain and normalized electrical resistances under cyclic elongation of 30% for a PPy-pTS film: The measurements for buckled Au, buckled PPy-pTs, and 2D buckled PPy-pTS films are marked with triangles, circles, and squares, respectively. Reproduced with permission. Copyright 2011, Wiley-VCH.^[36] Cross-section image of the fabric (unaltered) under d) 0% strain and e) 100% strain, respectively. f) Optical images of the battery under 0% strain [scale bar = 1 cm] and 100% strain [scale bar = 1 cm]. Reproduced with permission. Copyright 2012, Wiley-VCH.^[18b] g) Upon being stretched, the 2D Cu coil exhibits excellent extensibility because of the hierarchical spiral structures. As the Li metal is segmented into small domains separated by highly elastic SEBS rubber, the rubber absorbs the mechanical energy, whereas the electroactive Li domains are not affected. After the external stress is released, the extended SEBS rubber exerts a contraction force on the Li metal, allowing the whole electrode to recover its original shape and dimensions. h) Photographs showing the stretchability of the stretchable electrode: (left) original state; (right) 60% strain. Reproduced with permission. Copyright 2018, Elsevier.^[18c]

as shown in Figure 3g.^[18c] The stretchable metal anode was fabricated by electroplating Li metal onto a Cu coil as a current collector and poly(styrene-*b*-ethylene-*b*-butadiene-*b*-styrene) (SEBS) elastomer; the resulting the electrode maintains its electrochemical performance under a high level of strain (60%) (Figure 3h).

2.1.3. Hybrid Nanocomposite-Based Materials

A hybrid nanocomposite electrode material typically consists of a nanostructured rigid filler with good electrical properties and an elastomeric polymer with high stretchability.^[38] The elastomers, which include PDMS, polyurethane (PU), SEBS, and SIBS, have been widely used as a stretchable substrate for hybrid polymer composites. Because one-dimensional conductive materials such as CNTs and silver nanowires (AgNWs) can retain their electrical percolation network well under physical strain, they have commonly served as conducting fillers.^[39] Researchers have designed a sandwich-type polymer composite with a wavy layout for stretchable LIBs, as shown in Figure 4a.^[18d] Aligned CNT sheets mixed with active materials were transferred to a pre-strained PDMS substrate (i.e., strain of 450% in

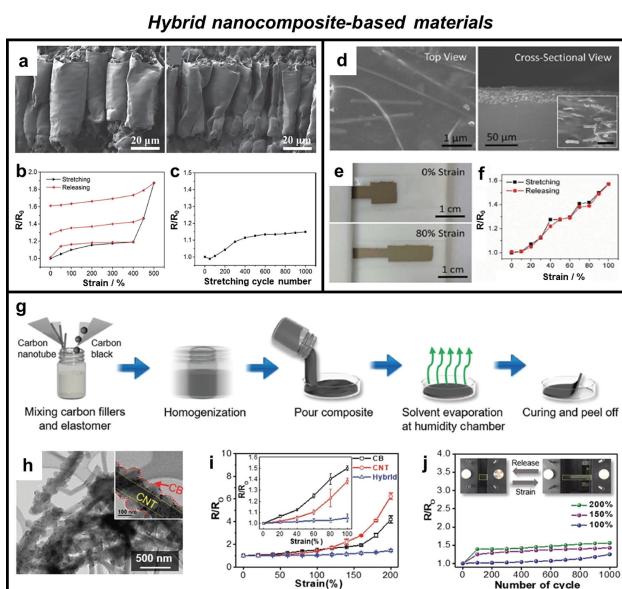


Figure 4. Hybrid materials for stretchable batteries. a) Enlarged views of the arched structure before (left) and after (right) 1000 stretching cycles at a strain of 400%, respectively. b), c) Dependence of the normalized resistance of LTO areal mass density of 5 mg cm^{-2} on stretching strain (b) and stretching cycle number (c). Reproduced with permission. Copyright 2015, Wiley-VCH.^[18f] d) Top view and cross-sectional view of the AgNWs embedded in a PDMS matrix. The inset in (right) is an enlarged cross-sectional view. Scale bar: 2 μm . e) The electrode stretched to 80% strain. f) Resistance change upon stretching and releasing of the electrode. Reproduced with permission. Copyright 2014, Wiley-VCH.^[40] g) Schematic showing the sequences in the overall fabrication process. h) TEM images of the HCP composite with different weight ratios of CB:CNT = 1:2. i) Normalized sheet resistance (R/R_0) of each composite film under different amounts of strain. j) Normalized resistance of the HCP composite under strains of 100%, 150%, and 200% that were repeated for 1000 cycles. Reproduced with permission. Copyright 2018, Wiley-VCH.^[18m]

the uniaxial direction) to fabricate stretchable electrodes. The obtained wavy electrodes exhibited high stretchability up to 400% and superior electrical percolation properties (stable electrical resistance at 400% strain after 1000 stretching/releasing cycles) (Figure 4b and c). As another example, Lee et al. demonstrated a stretchable conductor composed of AgNW networks embedded in a PDMS polymer matrix in Figure 4d.^[40] The stretchable conductor played a bifunctional role as both an active material and current collector. This elastic conductor exhibit stretchability of over 80% strain without any damage and exhibited stable electrical conductivity under 100% strain (Figure 4e and f).

Park and coworkers proposed a bio-inspired Jabuticaba-like stretchable hybrid polymer composite as a stretchable current collector comprising a hybrid carbon conductive fillers and a silicone rubber (Ecoflex).^[18m] Figure 4g depicts the fabrication procedure for their hybrid carbon polymer (HCP) composite. Figure 4h demonstrates that the hybrid carbon conductive fillers form a self-assembled structure in the polymer matrix, as observed by transmission electron microscopy (TEM), which effectively helped to maintain an intact electrical pathway under strain. The as-prepared HCP composite based on a simple and cost-effective solution process exhibited outstanding electrical properties of $1.4 R/R_0$ (R is the resistance of the

composite under various strains, R_0 is the resistance of the composite under initial strain) even at 200% strain, as shown in Figure 4i. Furthermore, the electrical percolation network of the composite showed superior durability after 1000 stretch/release cycles at a strain of 200% (Figure 4j). Interestingly, through in-situ small-angle X-ray scattering (SAXS) measurements, the authors demonstrated how the change in the orientations and interconnected network of the conductive fillers affected the electrical conductivity under strain. Their results demonstrate that in-situ SAXS analysis can provide profound insight into the behavior of conductive fillers in a polymer matrix under strain.

2.1.4. Conducting Polymers

In addition to the aforementioned materials, conducting polymers as the stretchable electrode materials for various battery systems have been intensively explored owing to their a high electrical conductivity, cost-effective, environmental compatibility and high theoretical capacity.^[41] Wallace group proposed buckled stretchable electrode based on p-toluenesulfonate anion (PPy-pTS) dopant (Figure 5a).^[36] The stretchable

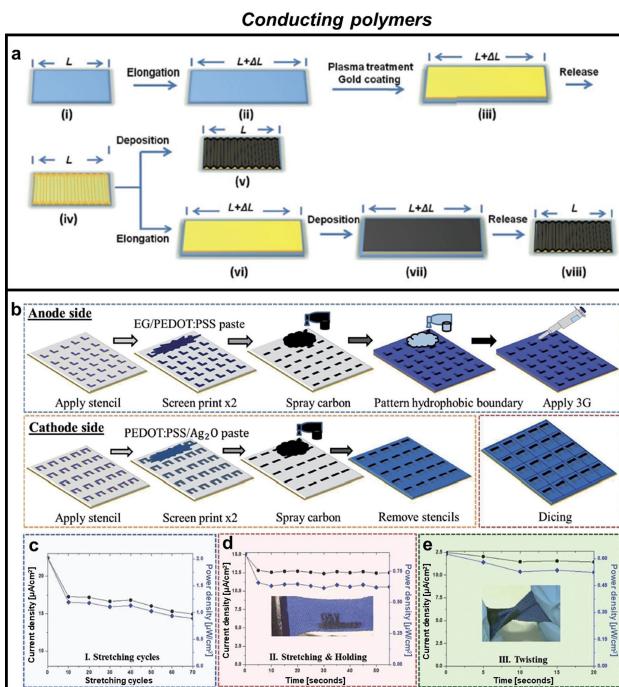


Figure 5. Conducting polymer for stretchable batteries. a) Schematic illustration showing the fabrication process of buckled Au or PPy-pTS films on SIBS substrate. The fabrication processes of buckled PPy-pTS conatin surface treatment, Au sputter coating, relaxation of the pre-strained SIBS substrate and PPy electrodeposition. 2D buckled PPy-pTS film was electrodeposited on the re-elongated Au coated substrate. Reproduced with permission. Copyright 2011, Wiley-VCH.^[36] b) Schematic illustration showing the batch-fabrication process of 35 individual MFC devices on a single textile layer. MFC device performances c) during repeated 70 cycles of 50% stretching, d) 50% stretching and holding for one minute, and e) twisting deformation; twisting and relaxing are repeated for every 5 s. Reproduced with permission. Copyright 2018, Wiley-VCH.^[42]

PPy-pTS electrode, which was ascribed to the pre-strain configuration, exhibited not only stable electrical conductivity under strain but also outstanding mechanical properties. In their work, stretchable Mg batteries composed of the buckled PPy-pTS cathode and Mg anode showed an operating voltage of 1.12 V after 2000 cycles under 30% strain condition. Furthermore, the proposed Mg battery system has been a promising candidate as a power source for implantable devices because these battery elements were biocompatible materials. Very recently, Choi and coworkers demonstrated stretchable microbial fuel cell (MFC).^[42] For the fabrication of anodic chamber, ethylene glycol (EG)-modified and 3-glycidoxypropyl-trimethoxysilane were introduced into poly(3,4-ethylenedioxy-thiophene):polystyrene sulfonate (PEDOT:PSS) to improve the electrical conductivity (~50 Ω/sq., sheet resistance) and hydrophilicity of the chamber. The mixture of PEDOT:PSS and silver oxide/silver was prepared to a cathodic chamber. Figure 5b shows a schematic illustration concerning the fabrication processes of the stretchable electrodes. As a result, the single MFC assembled by anode and cathode showed a maximum power density of 6.4 μW cm⁻². Furthermore, the MFC demonstrated stable power density even under various deformation conditions such as stretching and twisting states as shown in Figure 5c–e.

To date, carbon-based materials, metal-based materials, hybrid nanocomposite-based materials, conducting polymer are the four main options for fabricating a stretchable electrode. Each type of material exhibits advantages and disadvantages. For example, carbon-based materials possess a high surface area and are light weight, which tends to increase the specific capacity of batteries, but exhibit low electrical conductivity, which might adversely affect battery performance. Metal-based materials intrinsically have not only high electrical conductivity but also high energy density, which increases power density and energy density; however, uncontrollable growth of metal dendrites during charge/discharge processes induces harsh safety issues and severe cycle degradation. Hybrid polymer composite features a simple fabrication and cost-effective manufacturing process, but exhibits low electrical conductivity. Furthermore, conducting polymer with intrinsic stretchability and biocompatible properties demonstrates its potential application in stretchable electrode. However, it presents low electrical conductivity.

2.2. Electrolyte and Separator Membrane Materials

The electrolyte and the separator membrane are critical components in terms of safety in all battery systems. The electrolyte plays an important role as an ion-conduction medium, and the separator membrane is used to prevent physical and electrical contact between both electrodes.^[43] In a stretchable system, these parts become more important because they should be capable of being stretched without loss of their original functions that are closely related to safety. Accompanying the increased development of various types of stretchable batteries, suitable electrolytes, or stretchable sepa-

rator membranes are required. In general, solid-state electrolytes, solid polymer electrolytes (SPEs), and gel polymer electrolytes (GPEs) have been used instead of stretchable separator membranes because they are easily controllable and sufficiently deformable.^[44] Stretchable separator membranes have seldom been investigated because of the difficulty associated with fabricating a porous membrane with a high stretchability, high ion transport ability, and good wettability. In this section, recent developments in a solid-state electrolyte and stretchable separator membrane for stretchable batteries are discussed.

2.2.1. Solid-State Electrolytes

The traditional organic liquid electrolytes (e.g., Li salt in carbonate-based electrolyte) used in LIBs are not suitable for stretchable battery systems because of risks of leakage and a lack of mechanical stability. For the safe use of stretchable systems, flexible polymer electrolytes such as SPEs and GPEs have been developed in recent years. In the case of SPEs, the risk of liquid leakage is alleviated by substitution of the organic liquid in a traditional electrolyte with a solid ion-conducting material. Unfortunately, such SPEs exhibit low ionic conductivities (< 10⁻⁴ S/cm) at room temperature, leading to low battery performance.^[45] Also, poor mechanical properties restrict the application of SPEs in flexible/stretchable energy devices.

Kammoun et al. reported a flexible solid polymer nanocomposite electrolyte with a polyethylene oxide (PEO) matrix containing 1 wt% GO.^[46] This electrolyte showed high ionic conductivity and mechanical properties compared with those of pure PEO. The GO-containing SPE exhibited enhanced safety and thermal stability, as shown in Figure 6a and b. When the GO-containing SPE was used as a solid electrolyte in a spiral battery, the battery showed robust mechanical stretchability over 9000 stretching cycles and stable electrochemical properties after 100 cycles at ~650% out-of-plane deformation. Recently, Zamarayeva et al. developed a polyvinyl alcohol (PVA)-based polymer electrolyte containing KOH along with a cellophane layer that protects the PVA separator and Zn anode from oxidation in Zn–Ag batteries, as shown in Figure 6c and d.^[18j] They fabricated a unique serpentine-shaped Zn–Ag batteries that can be stretched to a tunable degree and with tunable directionality while maintaining its specific capacity. The PVA polymer electrolyte enhanced the mechanical properties of the battery by providing a flexible support for the Zn electrode and by delocalizing the stress experienced by the electrode. However, most of SPEs reported in the literature exhibit poor tensile properties because of their rigidity, indicating that they are unsuitable for stretchable battery systems.

GPEs possess higher ionic conductivities and greater mechanical deformability than SPEs. In general, small organic molecules of ethylene carbonate (EC) and dimethyl carbonate (DMC) are used in GPEs, in which they improve the transferability of Li-ions. Furthermore, GPEs show good self-standing characteristics through the combination of an appropriate polymer matrix, organic solvents, and Li salts that interact well

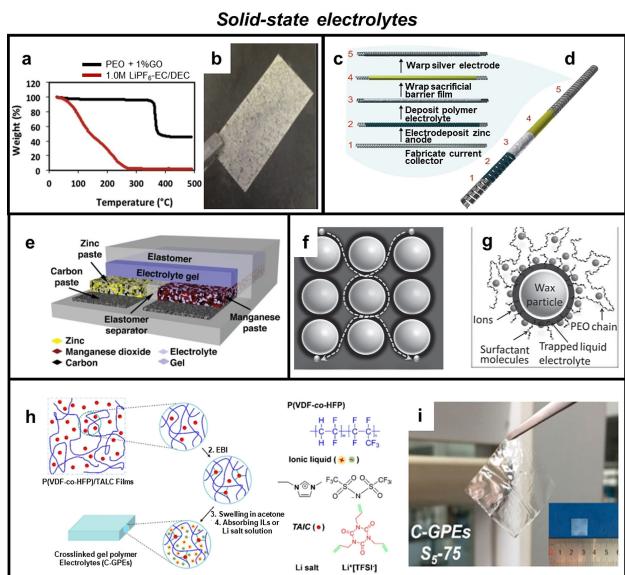


Figure 6. Solid-state electrolytes for stretchable batteries. a) TGA test of the solid PEO/1%GO compared with a commercial organic liquid electrolyte. b) An image of the PEO/1%GO mechanically stable, freestanding film. Reproduced with permission. Copyright 2016, Elsevier.^[46] c) The assembly flow diagram for the d) flexible wire-shaped batteries achieved by shaping the current collector-electrode as a helical band spring. Reproduced with permission. Copyright 2017, AAAS.^[18j] e) Scheme of a compliant zinc carbon dry gel cell. The cell is based on pastes as electrodes, chemically active cells, and an electrolyte gel to close the circuit. Intermixing and short-circuiting of the electrochemical power supply are prevented by laterally separating the electrodes with an elastomer separator. Reproduced with permission. Copyright 2010, Wiley-VCH.^[18a] f) Schematic image of the network structures designed for the gummy electrolyte. g) Details of the designed core-shell particles. Reproduced with permission. Copyright 2013, Wiley-VCH.^[47] h) Preparation of P(VDF-co-HFP)/TAIC blend films and cross-linked gel polymer electrolytes (C-GPEs). i) Photographs of samples before and after immersion in the ionic liquid. Note that the inset is a photograph of the sample before the immersion process. Reproduced with permission. Copyright 2017, American Chemical Society.^[50]

each other. Kaltenbrunner et al. prepared ultracompliant dry gels containing xanthan-gum-based gel electrolyte using a highly stretchable acrylic elastomer (3M VHB tape).^[18a] They used the xanthan gel to prepare a paste used in two electrodes, which can be deformed and stretched. These highly stretchable gel electrodes, as shown in Figure 6e, demonstrated good performance when subjected to 100 cycles of 20% strain. Wang et al.^[47] proposed a more innovative approach of creating a unique gummy hybrid electrolyte consisting of multiple-network structures using ultrahigh-molecular-weight PEO and core-shell particles with a liquid electrolyte (lithium perchlorate (LiClO_4) in propylene carbonate), as shown in Figure 6f and g. This gummy electrolyte showed a high ionic conductivity of $3 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature and almost defect-free contact with electrode materials, implying that it can wet the electrode surface very well. More interestingly, they adopted thermally sensitive wax particles as a core material; thus, the ionic conductivity of the gummy electrolyte began to decrease near the melting temperature of the wax particles, providing thermal protection.

Even though GPEs are highly recommendable candidates for ionic transport media and separator materials between two

electrodes in deformable energy devices, the mechanical strength of GPEs is very poor because of the presence of organic solvents. One way to solve this problem is a high degree of crosslinking of the polymer network. Choudhury et al. developed a gel polymer electrolyte based on cross-linked poly(epichlorohydrin) terpolymer (GECO) with a liquid electrolyte,^[48] resulting in an efficient increase in tensile modulus (0.6 MPa) and high ionic conductivity ($2.4 \times 10^{-4} \text{ Scm}^{-1}$) at room temperature. Although cross-linked GPEs (C-GPEs) with high mechanical robustness demonstrated its potential as an electrolyte for stretchable batteries, they used a flammable and volatile organic solvent that can cause safety issues. To solve these challenges, ionic liquids (ILs) have been proposed as solvents for electrolytes in recent years because of their advantages of nonvolatility, nonflammability, and safety.^[49] Recently, stretchable C-GPEs have been fabricated through electron-beam irradiation of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-co-HFP)]/triethyl isocyanurate (TAIC) blend films followed by adsorption of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][TFSI]), as shown in Figure 6h and i.^[50] The prepared C-GPEs had a high ionic conductivity of 1.4 mScm^{-1} at room temperature, a high tensile strength of 10.6 MPa, and an excellent elasticity, with almost full strain recovery after 100% stretching.

2.2.2. Stretchable Separator Membranes

Although ion-conducting GPEs can be used as both the electrolyte and the separator in batteries simultaneously, they possess intrinsically lower ionic conductivity than liquid electrolytes and inferior mechanical properties compared with those of stretchable separator membranes. Some authors have reported an internal shorting problem due to direct contact between the electrodes under physical deformations.^[51] To fabricate a reliable stretchable energy-storage device without these limitations, a physical separation barrier with an ion-conducting channel and stretchability is essential for a stretchable power source. Liu et al. developed new stretchable sticky PU/PVDF separator using an electrospinning method.^[18k] This PU/PVDF separator is highly porous, stretchable, and chemically stable, providing fast Li-ion transport and good electrochemical performance, as shown in Figure 7a and b. In addition, this good stretchability of PU/PVDF can avoid its breakage and detachment under repeated stretch/release cycles when used in a stretchable LIBs. Even though this sticky separator has worked well for the deformable batteries, the electrospinning process has critical drawbacks, such as the use of complex equipment, a slow production rate, and poor suitability for large-scale industrial production because of its high cost.^[52]

Park et al. first demonstrated a stretchable separator membrane for deformable energy-storage devices via a facile and scalable nonsolvent-induced phase separation (NIPS) method, as shown in Figure 7c.^[53] The NIPS process is one of the most promising fabrication methods for various porous membranes such as those used in energy-storage devices.^[54] This special separator membrane resulted in high stretchability

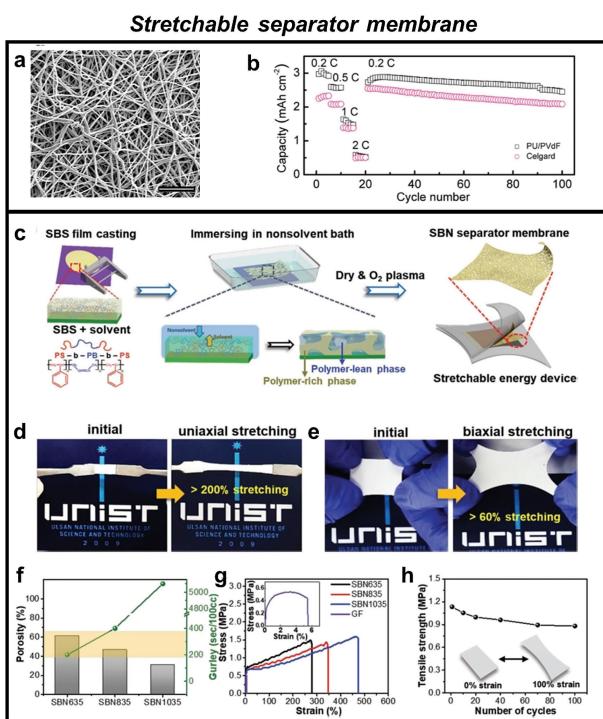


Figure 7. Stretchable separator membranes in stretchable Li^+ -ion batteries. a) SEM image of the PU/PVDF separator. Scale bar: 10 μm . b) Rate capability for the LCO/graphite full cell using Celgard separator and the PU/PVDF separator. Reproduced with permission. Copyright 2017, Wiley-VCH.^[18k] c) Schematic of the overall fabrication process based on the NIPS method. Digital photographs of the SBN separator membrane under d) uniaxial stretching and e) biaxial stretching. f) Changes in the porosity and the Gurley value of the SBN separator membrane with different polymer concentrations; highlighted range is the desirable porosity and Gurley values of the separator for typical LIBs. g) Stretchability test of each SBN separator membrane. The inset shows the mechanical properties of the GF. h) The tensile strength of the SBN635 separator membrane as a function of repeated strain cycles. Reproduced with permission. Copyright 2018, Wiley-VCH.^[53]

(270% in the uniaxial direction, 60% in the biaxial direction) and a high porosity of 60%, as shown in Figure 7d and e. Park et al. adopted poly(styrene-*b*-butadiene-*b*-styrene) (SBS) block

copolymer, which is a thermoplastic elastomer with a high stretchability and recyclability, and varied several key parameters of NIPS for tailoring the porosity and mechanical properties of the separator membrane, as shown in Figure 7f-h. When this separator membrane was used in stretchable LIBs subjected to 100% strain, the LIBs exhibited excellent cycling performance at a rate of 1 C for 100 cycles, implying that the separator membrane provided an effective physical barrier to prevent electrical contact between the electrodes and the ionic conduction channel.

Despite the study of these electrolytes and separators being in an early stage compared with the study of stretchable electrode materials, these early investigations provide insights that facilitate the development of stretchable solid-state electrolytes with high ionic conductivity and mechanical robustness, leading to stretchable separator membranes with high elastic and stable performances. Several recent developments in both electrolytes and separators, as previously discussed, are summarized in Table 1.

3. Structural Designs for Stretchable Batteries

Using the aforementioned materials, researchers have developed various stretchable batteries. However, stretchable batteries based on such materials still have some limitations imposed by their low stretchability. The following three major structural engineering strategies toward the design of stretchable batteries with high electrochemical performance and good mechanical properties have been proposed: wavy structures, island-bridge structures, and origami/kirigami structures.

3.1. Wavy Structures

The wavy structure, also known as the buckled structure or a pre-strain structure, is a well-known approach for achieving stretchable electronic devices such as energy-storage and conversion devices, implantable devices, stretchable solar cells,

Table 1. Summary of materials and performances in recently developed solid-state electrolytes and stretchable separator membranes.

Materials	Material performance Stretchability %	Cell type	Cell performance		Ref
			LIBs	Cell test	
SPEs	PEO + 1 % GO	–	1300 (out-of-plane)	Zn–Ag batteries	650% out-of-plane deformation [46]
	PVA + KOH	–	100	Zn–MgO ₂ batteries	20 cycles with 100% strain [18j]
GPEs	Xanthane gel PEO + Wax particles	– 3×10^{-4}	100 arbitrary deformation	–	– [18a] [47]
	Cross-linked polyepichlorohydrin terpolymer	2.4×10^{-4}	800	Li–S batteries	50 cycles without strain [48]
Separators	Cross-linked P(VDF-co-HFP)	1.4×10^{-4}	300	LIBs Li/LFP half cell	90 cycles without strain [50]
	PU + PVDF	–	100	LIBs LCO/Graphite	60 cycles with 50% strain [18k]
	SBS	–	100	LIBs LFP/LTO	100 cycles with 100% strain [53]

and stretchable displays.^[55] This geometric configuration can accommodate a high degree of physical strain by changing the wave amplitudes and wavelength to avoid destroying the device performance.^[56] Wavy structures are normally fabricated via the following steps; i) the rigid materials (e.g., metals, semiconductors, and active materials) are transferred to a pre-strain elastic substrate (e.g., PDMS, PU, and Ecoflex) using chemical or physical bonds; ii) the applied strain on the substrate is released. Releasing the strain makes the elastic substrate return to its unstrained state and form periodic wavy configurations. The difference in thickness and elastic modulus between the rigid material and the substrate and the degree of pre-strain of the elastic substrate determine the wavelength and amplitude of the wave, which can influence the stretchability, long-term stability, and surface roughness of the wave structure.^[57]

Many researchers have demonstrated stretchable batteries with this wavy configuration. Recently, Cui et al. proposed fully stretchable LIBs based on the macroscopic level of wavy configuration.^[18k] Figure 8a shows conventional rigid battery components such as electrodes, an separator membrane, and packaging materials imparted with stretchability using a millimeter-sized wavy structural layout, which guarantees high mechanical stretchability and durability. In this study, the authors focused on adhesion properties between several component layers when an external force was applied to the batteries. The elastic-sticky separator membranes not only suppress delamination of the components and crack generation under strain but also improve mechanical properties. The full batteries demonstrated a high areal capacity of 3.6 mAh cm^{-2} and outstanding energy density as high as 172 Wh L^{-1} . Furthermore, the batteries well sustained their electrochemical performance after multiple cycles under 50% strain. In addition, Kaltenbrunner and coworkers designed stretchable Zn–MnO₂ batteries based on the wave configuration (Figure 8b). The

buckled Au current collector was suspended into an elastomer matrix, which could accommodate substantial mechanical stress in the electrode materials during repeated stretching cycles without obvious damage to the structure (Figure 8c).^[58] A hydrogel was simultaneously used as both an electrolyte and an elastic separator membrane to improve the adhesion properties between battery component layers. The stretchable gel electrolyte exhibited decreased interfacial resistance and improved electrochemical performance (with a high areal capacity of 1.6 mAh cm^{-2}), as shown in Figure 8d and e. Moreover, the batteries could be stretched as much as 50% without degradation of device performance. However, the wavy structure makes the device surface very rough, resulting in difficulty of integration with other devices.

3.2. Island-Bridge Structure

Another efficient strategy to design stretchable electronics is island-bridge configurations composed of rigid island materials connected with highly conductive metal interconnections onto the elastomeric substrate. These islands and bridges are patterned in various methods such as lithography, mask evaporation, and so on.^[59] The bridges such as metal interconnection can maintain their electrical conductivity under large physical deformations without apparent defects in the structure.^[60] The stretchability is determined by the wavelength and amplitude of this interconnection. Rogers and coworkers have reported stretchable LIBs based on an island-bridge layout with self-similar serpentine interconnections (Figure 9a).^[18c] This configuration can be used in highly stretchable batteries, where it ensures biaxial mechanical strain. Indeed, the mechanical stability of such battery interconnections was analyzed via finite element analysis. The metal interconnection attached to a polyimide (PI) layer exhibited high mechanical robustness, even up to 300% strain, while maintaining its electrical conductivity. Also, the batteries displayed an areal capacity as high as 1.1 mAh cm^{-2} , demonstrating stable output power even under a biaxial strain of 300% (Figure 9b and c). Using a similar structural layout, Zhong et al. fabricated stretchable Zn-air batteries with fiber electrodes and a hydrogel electrolyte; the batteries achieved stretchability as high as 100%.^[61] Figure 9d and e display stretchable batteries based on layer by layer construction. A serpentine-structured copper circuit wire was introduced to achieve high stretchability. The proposed stretchable Zn-air batteries were found to exhibit good stretchability up to 100% without failure of their device performance (Figure 9f). To improve energy density and operating voltage necessary for practical wearable devices, several Zn-air batteries were integrated together in series or parallel on a single device. Indeed, various serpentine-design strategies have provided a wide range of working voltages and output currents.

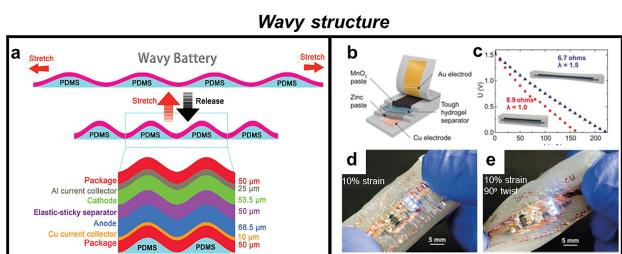


Figure 8. Wavy structure design for stretchable batteries. a) Schematic of the stretchable battery based on a device-scaled wavy structure and elastic-sticky separator. Note that all of the components, including the cathode and anode and package, are stretchable. Reproduced with permission. Copyright 2017, Wiley-VCH.^[18k] b) Scheme of a stretchable battery in top configuration, enabled by the tough hydrogel separator instantly tough-bonded to the elastomer matrix. Imperceptible 1.4-mm-thick electrodes serve as current collectors. Cu-coated PET foil with Zn paste is the anode, and MnO₂ paste contacted with Au-coated PET is the cathode. c) Voltage versus discharge current at 0% (red squares) and 50% (blue triangles) strain. The internal resistance decreases from 8.9 to 6.7 Ω with stretching due to thinning of the hydrogel separator. Stretchable circuit atop a hydrogel-based battery in d) relaxed and e) strained and twisted states, without degradation of performance. Reproduced with permission. Copyright 2017, American Association for the Advancement of Science.^[58]

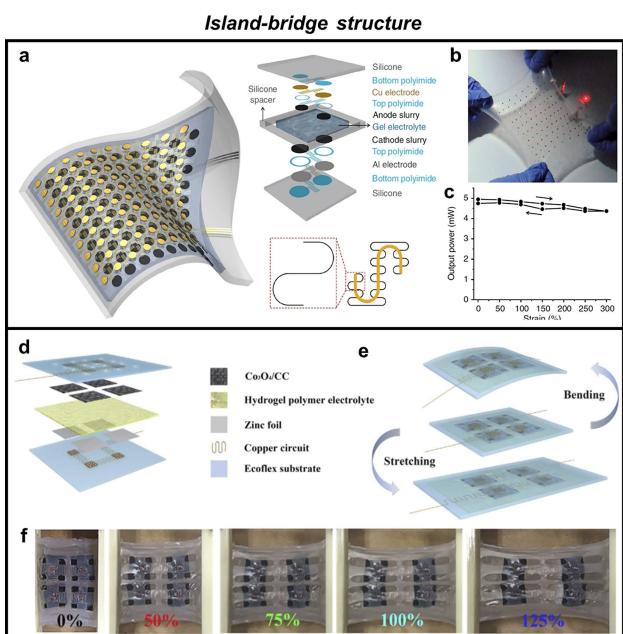


Figure 9. Island-bridge structure design for stretchable batteries. a) Schematic of a completed device in a state of stretching and bending; exploded-view layout of the various layers in the battery structure; illustration of "self-similar" serpentine geometries used for the interconnects (black: first-level serpentine; yellow: second-level serpentine). b) Operation of a battery connected to a red light-emitting diode (LED) while biaxially stretched to 300%. c) Output power as a function of the applied biaxial strain. Reproduced with permission. Copyright 2013, Macmillan Publishers Limited.^[18c] d) Exploded view of a multilayered structure of the planar stretchable/flexible Zn-air battery array. e) Schematic image of a completed Zn-air battery array depicted in a state of stretching or bending. f) Photographs of the stretchable, flexible Zn-air battery array stretched under 0%, 50%, 75%, 100%, and 125% strain. Reproduced with permission. Copyright 2017, Elsevier.^[61]

3.3. Origami/Kirigami Structure

The origami/kirigami structural layout is an additional strategy for fabricating stretchable batteries with high mechanical deformation without degradation of electrochemical performance. Basically, an origami structure is folded layer by layer and can be easily unfolded.^[62] A kirigami structure is similar but is fabricated via more complex processes involving cutting and then folding.^[63] Opinions differ as to whether these structures should be classified as stretchable batteries or just foldable paper batteries; however, in the present review, we will focus on stretchable batteries.

Jiang et al. reported stretchable batteries based on origami structural layouts (Figure 10a).^[18e] The origami structure enabled the conventional rigid materials to be used without large strain on the parallelogram facets, which are unfolded large sheets (Figure 10b). Predefined creases at the folded part made the device foldable and stretchable. An areal deformability of 1600% was achieved. The highly conductive ($< 5 \Omega$) and mechanically robust current collector was prepared by a simple dip-coating method in which porous paper with high flexibility was impregnated with a CNT solution. Active materials were then coated onto the flexible paper current collectors to fabricate entire electrodes. Origami LIBs were assembled using

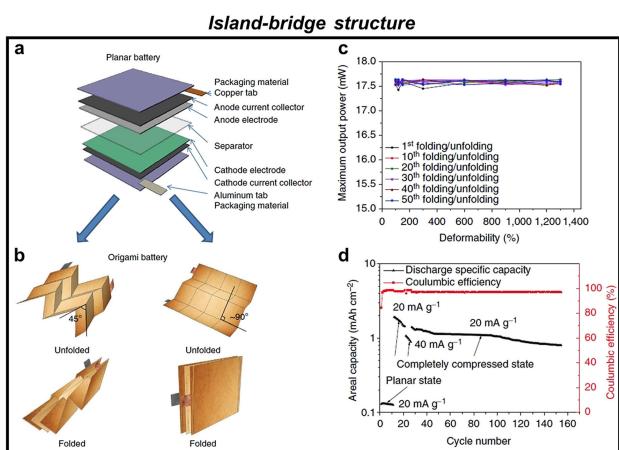


Figure 10. Origami structure design for stretchable batteries. a) Exploded view of the multilayer structure of conventional LIBs in the planar state. b) Two examples of origami LIBs using Miura folding. The lower left pictures refer to 45° Miura folding in the unfolded and folded states, showing that it can be completely compressed in one direction. The lower-right pictures refer to 90° Miura folding in the unfolded and folded states, showing that it can be completely collapsed in biaxial directions. c) Maximum output power of the origami LIB as a function of linear deformability over 50 cycles of folding and unfolding. d) Capacity retention (left axis, black) and coulombic efficiency (right axis, red) as a function of cycle number for two current densities, 20 and 40 mA g⁻¹. Reproduced with permission. Copyright 2014, Macmillan Publishers Limited.^[18e]

the desired origami patterns. In this design, the origami LIBs displayed an areal capacity of 2 mAh cm^{-2} when the batteries were completely compressed. Also, the batteries could withstand various severe mechanical deformations as high as 1600% without any change in the detectable output voltage (Figure 10c and d). A kirigami-structured battery was also reported by the same group. In this case, three different kirigami patterns such as zigzag-cut pattern, cut-N-twist pattern, and a cut-N-shear pattern were introduced to increase the deformability.^[18g] With these patterns, the kirigami batteries could achieve linear stretchability of 100%. The energy capacity of the batteries was approximately 30 mAh, and capacity retention was 85% after 100 cycles. The batteries could deliver a stable operating voltage of 3.83 V under a strain of 90% without suffering substantial device performance deterioration. Strain-engineered structures such as buckling, island interconnection, and origami structures have been widely explored for fabricating stretchable current collectors; however, surface roughness, a complex manufacturing process, and low long-term stability has limited their practical applications.

4. Stretchable Batteries

Stretchable materials and various structural engineering concepts have been used to demonstrate a various stretchable battery system with high stretchability and reasonable device performance. In this section, we cover recently reported stretchable batteries such as Li-based batteries, multivalent-based batteries, and metal-air batteries.

4.1. Li-based Batteries

Li-based batteries, including LIBs, Li-sulfur, Li–O₂, and ALBs, are based on Li-ion as charge carriers. Li possesses a low redox potential (−3.04 V versus SHE) and low atomic number, leading to a high specific energy density.^[64] Among the Li-based batteries, LIBs are considered as one of the most promising energy-storage systems for use in stretchable batteries because of their lack of a memory effect, high energy density, and mature technology. Stretchable LIBs are also fabricated with key components, such as a cathode, anode, separator, and electrolyte. These components are normally vulnerable to mechanical deformation.^[65] Thus, designing materials and developing fabrication structural strategies are important for achieving reliable stretchable LIBs that can maintain their performance under external influences.

Bao and Cui's group designed a carbon/silicon/polymer foam as a stretchable anode through a wave/buckling process, as shown in Figure 11a.^[18h] The outer layer of the electrode consisted of a highly elastic self-healing polymer a mixture of fatty acid dimers and trimers reacted with diethylenetriamine (DETA) that helped to maintain its electrochemical performance during the stretch/release process. To investigate stable stretching properties of the polymer layer of the foam electrode, the researchers subjected the electrode to 1000 cycles under 25% strain and then measured the resistance upon cycling (Figure 11b). The resistance eventually increased, but the value was sufficient for the material to be used as a battery electrode (<

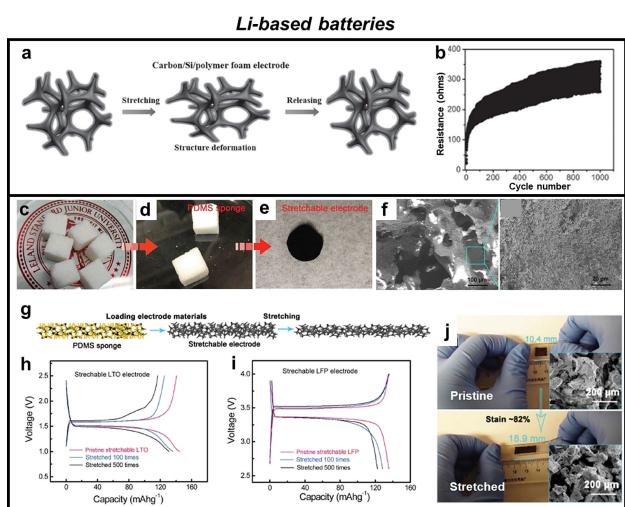


Figure 11. The design strategy of stretchable Li⁺-ion batteries. a) Schematic of a stretching and releasing process for a carbon/Si/self-healing polymer foam electrode. b) Resistance measurements during strain cycling to 25%. Resistance increases over time. Reproduced with permission. Copyright 2016, Wiley-VCH.^[18h] Schematic of the synthesis of a stretchable electrode for LIBs. Digital photographs of c) sugar cubes, d) PDMS sponge, and e) the stretchable electrode. f) Cross-sectional SEM images of the stretchable electrode at (left) low and (right) high magnification. Reproduced with permission. g) Schematic illustration for morphological behavior of stretchable electrode based on the PDMS sponge. Discharge/Charge voltage profiles of stretchable h) LTO anode and i) LFP cathode with various stretch-release cycles. j) Digital photographs show the electrode with stretchability of ~82%. The inset images show SEM images of the electrode in unstretched state and stretched state, respectively. Copyright 2016, Wiley-VCH.^[66]

400 Ω after 1000 cycles). Thus, the elastic polymer layer maintained good overall electrode contact as the external force was applied.

An organic framework has also been proposed as a method to fabricate stretchable electrodes.^[66] Sugar cubes as a pore-creating agent were used as scarifying agents to design 3D porous sponge-like PDMS scaffolds with high stretchability. The as-fabricated PDMS sponge was then filled with a blend of active material, carbon black, and binder to fabricate stretchable electrodes, as shown in Figure 11c–e. SEM images of the as-synthesized electrodes (Figure 11f) show homogeneous loading of the electrode materials participating in the electrochemical reaction in the porous 3D PDMS sponge, which imparts stretchability to the whole electrode. That is, the PDMS sponge combined with electrode materials promoted stretching durability, as depicted in the schematic in Figure 11g. The active materials loaded onto stretchable electrodes actually agreed well with the electrochemical results; 91% and 82% of the capacity before stretching was retained after 5000 stretch/release cycles for electrodes with LTO and LiFePO₄ (LFP) active materials, respectively, as shown in Figure 11h and i. Furthermore, the PDMS sponge retained its original structure without critical damage to the morphological structure of the electrodes even though the electrode was stretched with 82% strain (Figure 11j).

Likewise, various conceptual stretchable LIBs have recently been reported to materialize practical battery design with high electrochemical performance even under mechanical deformation. Peng et al. suggested a gum-like super-stretchy battery with a multilayered structure, as described in the previous section.^[18f] Each layer is designed with an arched anode (elastic substrate and CNT/LTO-CNT), an arched cathode (elastic substrate and CNT/LMO-CNT), gel electrolyte, and an elastic polymer wrap for stretchable battery system. The arched structure of the electrodes is important for their ability to undergo stretching and deformation while maintaining their electrochemical properties. Interestingly, the output energy remains stable, with a capacity retention of 97% after 200 stretch/release cycles under 400% strain (Figure 12a). Even after several hundred deformation cycles, the battery exhibited good performance, showing 87% capacity retention after 100 charge/discharge cycles with almost 100% coulombic efficiency, as shown in Figure 12b. Figure 12c demonstrates the dynamically outstanding structural stability of a gum-like super-stretchy battery. The battery was subjected to a 400% stretch/release process at high speed (3 cm s^{−1}). When the battery was discharged at 1 C and reached the discharge plateau at approximately 2.5 V, the voltage fluctuation during the test was less than 1%. Furthermore, the photograph in Figure 12d shows that a real battery composed of gum-like LIB maintains a steady intensity of LED power when stretched with increasing strain to 400%.

To achieve stretchability and mechanical strength, Cui and coworker also suggested a new battery assembly design with a wavy structure and an elastic/sticky separator composed of PU/PVDF polymers (Figure 12e).^[18k] The discharge/charge voltage profiles of the assembled LCO/graphite wavy battery with good

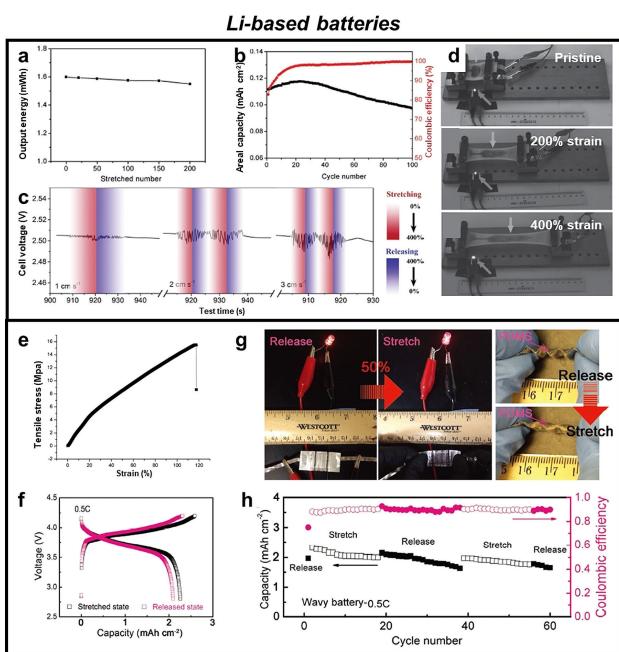


Figure 12. Electrochemical performance for various conceptual stretchable batteries. a) Dependence of the output energy on stretching cycle number. b) Long-life performance of the battery after 200 stretching cycles. c) Voltage profiles when discharging at 1 C under stretching/releasing at increasing stretching/releasing speeds. d) The gum-like LIB lighting up an LED without stretching, and under stretching with increasing strains of 200% and 400%. Reproduced with permission. Copyright 2015, Wiley-VCH.^[18f] e) Tensile stress vs. strain for the PU/PVDF composite separator. f) Discharge/charge voltage profiles of a wavy battery at stretched and released states. g) Digital photographs of the wavy battery powering a light-emitting diode at the released state and the stretched state at 50% strain. Photographs showing that, when stretching the wavy battery, PDMS was stretched to accommodate the deformation. h) Cycling performance and coulombic efficiency for the wavy battery under releasing and stretching states (50% strain). Reproduced with permission. Copyright 2017, Wiley-VCH.^[18k]

mechanical properties of this well-made separator showed a similar areal capacity of approximately 2.2 mAh cm^{-2} even after stretching/releasing manipulation (Figure 12f). This result clearly indicates that the elastic/sticky polymer can alleviate mechanical stress and maintain a constant attachment with both the cathode and the anode during deformation. Further, the wavy battery demonstrated practical feasibility in the dynamic state, as shown in Figure 12g. The battery continuously powered an LED device during repeated stretching/releasing with 50% strain. In addition, stable electrochemical behavior was observed, which corresponds to 85% capacity retention with a high areal capacity of 1.65 mAh cm^{-2} even under 50% strain at 0.5 C for 60 cycles (Figure 12h).

In this section, we show the design concept and electrochemical performance of reported recently stretchable LIBs. Although great advances have been achieved in stretchable LIBs, the desired performance level for reliable wearable devices has not been achieved. For example, stretchable LIBs based on wavy and serpentine structural engineering demonstrated outstanding stretchability and electrochemical performance. However, these fabrication steps are usually complicated, causing an increase in manufacturing cost. To address this

limitation, researchers should devote more attention to establishing a simple and novel fabrication process. Moreover, to improve the energy density of the stretchable batteries, new active materials that can accommodate mechanical strain, such as a polymeric organic active material, should be explored.

4.2. Multivalent-Based Batteries

Although LIBs are a promising candidate as a stretchable battery system, they are problematic with respect to potential environmental harm, high cost, and intrinsic safety issues.^[67] These limitations are critical issues in wearable electronics because they are operated in direct contact with the human body.^[68] Many researchers have investigated replacing Li-based batteries with other metal-ion batteries to overcome the aforementioned issues. Such metal cations can be divided into two groups, monovalent metal cations (Na^+ and K^+) and multivalent metal cations (Mg^{2+} , Al^{3+} , Ca^{2+} , and Zn^{2+}), depending on the oxidation states of the metal ions.^[69] One of the substitutes is Na-ion batteries because those alkali materials are cost-effective materials. Besides, as Na-ion is monovalent cation, it exhibits analogous electrochemical property compared to Li-ion. For example, Yu group demonstrated all-stretchable Na-ion batteries.^[18l] Their battery system worked functionally even in 50% stretched state and could turn on the typical LEDs in diverse mechanical deformations. Compared with monovalent metal cations, multivalent metal cations theoretically possess greater electrochemical energy-storage capability by enabling multiple-electron transfer.^[70] Recently, Wallace et al. reported the stretchable Mg-ion micro-size bio fuel cell, which delivered low electrochemical performance compared with other battery system.^[36] Zn-based battery system is the most vigorously studied system among multivalent metal cation-based batteries because they exhibit advantageous properties such as their compatibility and high chemical/electrochemical stability in an aqueous system coupled with facile charge/discharge, low toxicity, low cost, and environmental friendliness.^[71]

Stretchable Zn-based batteries, such as Zn–Ag, Zn– MnO_2 , Zn–NiOOH, and Zn-air, have been fabricated using novel structural designs (e.g., wire and serpentine layouts), diverse materials (e.g., polymer composites and hydrogel electrolytes), and fabrication processes (e.g., printing technologies and electroplating). In 2010, Bauer and coworkers reported a stretchable dry cell in which a zinc paste anode and a manganese paste cathode were fabricated on an elastic current collector (i.e., a carbon black and silicone oil paste membrane).^[18a] This dry gel battery system exhibited open-circuit voltages of approximately 1.5 V as well as a long-term cycling life greater than 1000 h and a capacity of 3.5 mAh cm^{-2} . In addition, the batteries could power an LED even under 100% uniaxial strain. However, when the batteries were stretched to 100%, minor cracks appeared on the electrode surface and the short-circuit current was reduced to less than half of its initial value (to $\sim 10 \text{ mA}$) after the first cycle. Nevertheless, their demonstration of a stretchable Zn-based battery system is noteworthy.

Steingart et al. fabricated stretchable Zn–MnO₂ batteries with a polyacrylic acid gel electrolyte.^[18b] To make the batteries stretchable, they embedded active materials (zinc anode paste and manganese dioxide cathode paste) into the stretchable wavy silver fabric that served as a current collector. The specific discharge capacity of the as-assembled cell was approximately 3.88 mA h cm⁻² in the initial strain state, and no decrease in the specific discharge capacity was detected at 100% strain. Bauer's group reported rechargeable stretchable Zn–MnO₂ batteries based on an acrylic elastomer.^[72] The open-circuit voltage (1.37 V) was maintained even at 50% strain, and the battery systems showed a power density of 1.93 mW g⁻¹. Also, the batteries retained 25% of their initial capacity after 80 cycles.

Stretchable Zn-based batteries combined with Ag metal as a cathode material have also been reported. Arias et al., for instance, reported stretchable Zn–Ag batteries based on a current collector with a novel structure called "serpentine ribbon layout," as shown in Figure 13a.^[18j] The specific areal capacity of the stretchable batteries was approximately 3.5 mA h cm⁻², and they well sustained their specific capacity stably during 500 stretch/release cycles at 100% strain (Figure 13b). Also, these novel-structured stretchable batteries exhibited little change in internal resistance during the stretching process, indicating good adhesion between the

active materials and a current collector at extreme physical deformations (Figure 13c). Additionally, Wang et al. proposed screen printing technologies as a facile and mass-production-compatible method to fabricate stretchable Zn–Ag batteries (Figure 13d).^[73] Conductive inks, which are mixed active materials with a poly(styrene-*b*-isoprene-*b*-styrene) (SIS) binder, were printed on a highly elastic polyurethane-spandex substrate. The introduction of the SIS binder not only enhanced the mechanical properties of the electrode but also prevented exfoliation of the conductive materials from the elastic substrate. These stretchable Zn–Ag batteries remained functional at 100% stretch and maintained their conductivity for 10 cycles in the stretched state. Compared with the resistance of the batteries in the pristine state, however, that of the batteries in the 100% stretched state was approximately 3.5 times greater (2.3 kΩ for the stretched state versus 0.65 kΩ for the pristine state). Figure 13e and f shows that, due to the increase of polarization, the average voltage drops of the batteries under strain and their discharge capacity decreased compared with initial state until 30 cycles.

Recently, Zhi et al. reported mechanically robust yarn-structured stretchable Zn–MnO₂ batteries composed of a Zn anode and an MnO₂ cathode with a polyacrylamide hydrogel electrolyte, as demonstrated in Figure 13g.^[18n] This elastic hydrogel could be stretched to 3000% strain and exhibited a high ionic conductivity of 1.65×10^{-2} S cm⁻¹. The stretchable Zn–MnO₂ batteries demonstrated a specific discharge capacity of 260.4 mA h g⁻¹ at a current density of 0.2 A g⁻¹. They showed an open-circuit voltage of approximately 1.48 V and a high volumetric energy density of 53.8 mWh cm⁻³. The yarn-structured batteries showed stable long-term cycling performance, including 98.5% of the initial capacity and a coulombic efficiency per cycle of nearly 100% for 500 cycles. In addition, they tolerated several mechanical deformations and exhibited high capacity retention of ~95% after 100 stretching cycles at 300% strain, as shown in Figure 13h and i. Accordingly, the stretchable yarn-based Zn–MnO₂ batteries with good electrochemical properties and mechanical robustness are promising for integration into stretchable textiles for reliable wearable electronics.

Advanced stretchable Zn-based batteries with high physical stretchability and stable electrochemical features have recently been developed; however, several limitations remain to be addressed to achieve their practical application in wearable devices.^[74] First, general Zn-based batteries exhibit low operating voltages because their aqueous electrolytes feature a narrow potential window (1.23 V). Xu et al. reported a "water-in-salt" battery system that expands the operating range of the aqueous electrolyte by using highly concentrated salt in the electrolyte.^[75] Meanwhile, Mai et al. reported Zn–V₂O₅ batteries with a high-salt-concentration system and enhanced operating voltage.^[76] However, a further increase of the operating voltage is required to develop electronics with maximized energy densities. This increase in operating voltage can be achieved by developing novel cathode materials that recharge in a higher-potential region and modified electrolytes that can function in wider voltage ranges. In addition, the formation of Zn dendrites

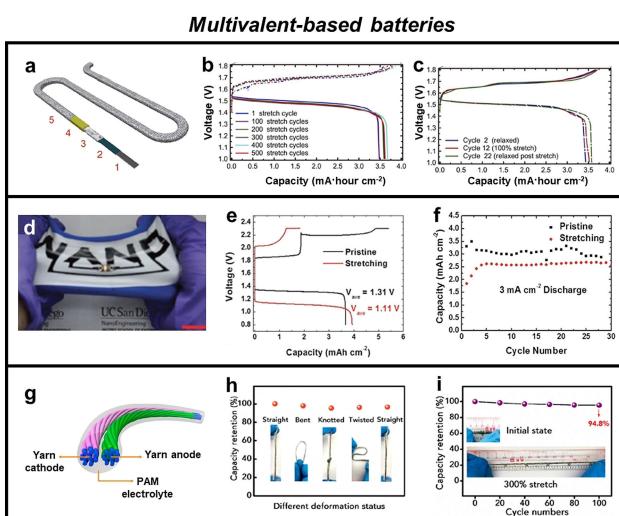


Figure 13. Structural design and electrochemical performance for different types of stretchable multivalent-based batteries. a) Stretchable serpentine-shaped batteries fabricated using the current collector of serpentine ribbon geometry. b) Galvanostatic charge-discharge curves for the electrochemical cycles following the 1st, 100th, 200th, 300th, 400th, and 500th stretching cycles of the battery. c) Galvanostatic charge-discharge curves for the 2nd (flat configuration), 12th (stretched configuration), and 22nd (flat configuration) electrochemical cycles of the battery. Reproduced with permission. Copyright 2017, American Association for the Advancement of Science.^[18j] d) Photograph of a sealed battery being biaxially stretched. e) The first cycle voltage profile of the stretchable battery cycled with 2 mA h cm^{-2} . f) The discharge capacity during prolonged cycled, cycled with 3 mA cm^{-2} . The stretched battery was subjected to 100% stretching 10 times before the electrochemical cycling. Reproduced with permission. Copyright 2016, Wiley-VCH.^[73] g) Schematic of the fabrication and encapsulation of the yarn ZIB. h) Capacity retention of the yarn ZIB under various deformation states. i) Dependence of the capacity retention on the cycle number with a strain of 300%. For (h-i), tests were performed at a current density of 0.3 A g^{-1} . Reproduced with permission. Copyright 2018, American Chemical Society.^[18n]

in the anode region is another drawback, leading to reduced cycle retention of Zn-based batteries due to inevitable short circuit problems.^[77] To suppress the growth of Zn dendrites, Jiang et al. introduced a porous carbon layer onto the Zn anode surface.^[78] The introduced porous carbon layer provides nucleation sites, preventing the growth of dendrites inside the battery. When a galvanostatic symmetrical cell consisting of a bare Zn electrode and a Zn electrode with a porous carbon layer ($Zn|Zn@C$) were tested, a short circuit occurred in the bare Zn cell, whereas the $Zn@C$ electrode showed settled cycling performance over 300 cycles at a charge/discharge rate of 2.5 mA cm^{-2} . The cycling stability of the $Zn@C$ was attributed to a uniform current flux, which led to the suppression of Zn dendrite growth.

Thus, even though Zn-based batteries have some remaining challenges, they are promising battery systems for deformable electronics such as wearable devices or soft electronics because of their various advantages (e.g., intrinsic safety, environmental friendliness, and simple fabrication processes). Therefore, Zn-based batteries are a good candidate for energy-storage systems for deformable devices if their fatal issues are solved.

4.3. Metal-Air Batteries

Recently, metal-air batteries, such as Li-air, Zn-air, and Al-air batteries have emerged as promising candidates to meet the demands of various devices such as electronic vehicles (EVs), portable devices, and wearable devices because of their high energy density, low cost, and environmental friendliness.^[79] Traditional metal-air batteries consist of a negative metal electrode (e.g., Li, Zn, and Al), porous air cathode membrane with catalyst, and an electrolyte (e.g., alkaline or aqueous electrolyte depending on battery chemistry).^[80] To achieve stretchable metal-air batteries for powering wearable devices, tremendous efforts have been devoted to developing battery structures and novel materials.^[81] From a structural point of view, a fiber-shaped battery design has various unique properties that are beneficial to wearable electronic devices.^[82] For example, fiber-type metal-air batteries could not only be woven into various forms of cloth but also easily integrated into a textile structure together with functional wearable devices such as sensors and electronics.^[83] These advantages make fiber-shaped stretchable metal-air batteries a favorable power accessory in the field of wearable electronics devices.

Peng et al. proposed stretchable fiber-shaped Zn-air batteries comprising a cross-stacked CNT sheet cathode for the oxygen reduction reaction (ORR), a RuO₂ catalyst for the oxygen evolution reaction (OER), and a Zn spring anode. In particular, the CNT sheet cathode serves as both a gas diffusion layer and a current collector.^[84] The Zn-air batteries exhibited stable discharge curves at a current density of 1 Ag^{-1} under 10% strain (Figure 14a). Peng's group also demonstrated all-solid-state stretchable fiber-shaped Al-air batteries for wearable devices, as presented in Figure 14b.^[18j] In this case, a spring-like Al metal piece that could provide stretchability of an intrinsic rigid metal was used as an anode. They prepared a gel

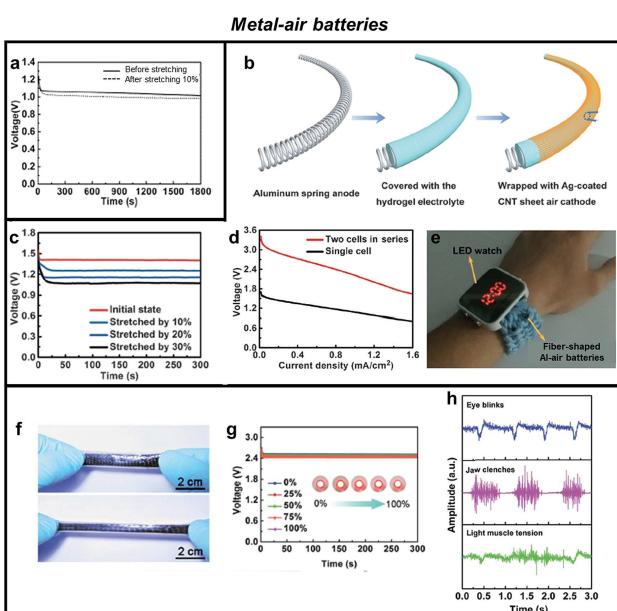


Figure 14. Structural design and electrochemical performance for different stretchable metal-air batteries. a) Discharge curves of the fiber-shaped Zn-air battery with a length of 10 cm at a current density of 1 Ag^{-1} before and after stretching by 10%. Reproduced with permission. Copyright 2015, Wiley-VCH.^[84] b) Fabrication of the fiber-shaped Al-air battery. c) Discharge curves of fiber-shaped Al-air batteries at different stretching ratios at a discharge current of 1 mA . d) Polarization curves of a single fiber-shaped Al-air battery and two batteries in tandem (scan rate 2 mV s^{-1}). e) Photograph of a commercial LED watch powered by two fiber-shaped Al-air batteries woven into a fabric and connected in series. Reproduced with permission. Copyright 2016, Wiley-VCH.^[18j] f) Flexibility and stretchability of the Li-air battery. Photographs of the stretchable Li-air battery before and after stretching. g) Discharge curves of the stretchable Li-air battery under increasing strains. The inset photographs display a red LED powered by the Li-air battery under increasing strains. h) Different physiological signals collected using a wearable physiological monitoring system. Reproduced with permission. Copyright 2016, Royal Society of Chemistry.^[85]

electrolyte consisting of KOH dissolved in a PVA/PEO polymer with ZnO and Na₂SnO₃ as additives. Their results demonstrated that the gel electrolyte with additive suppressed the corrosion of the Al metal anode in the alkaline electrolyte and also prevented an internal short circuit by the physical deformations. Using the gel electrolyte, the solid-state fiber-shaped Al-air batteries delivered a highly stable operating voltage of 1 V at a strain of 30% (Figure 14c). The stretchable fiber-shaped Al-air batteries were easily integrated with practical devices and successfully delivered power to an LED watch, as presented in Figure 14d and e.

Peng and coworker have demonstrated sandwich-type stretchable Li-air batteries to integrate with a wearable physiological monitoring system.^[85] The stretchable Li-air batteries were developed by combining rippled aligned CNT sheets with Li sheets attached to a pre-strained Cu array. A polymer gel electrolyte was selected as a solid electrolyte to produce solid-state stretchable Li⁺-ion batteries. The stretchable Li-air batteries were produced by sandwiching the gel electrolyte between a pre-strained anode and pre-strained cathode. As presented in Figure 14f, the stretchable Li-air batteries achieved a very high level of strain because of their pre-strained

structure. The discharge voltage of the stretchable Li-air batteries was well maintained after the batteries were stretched to 100%, without degradation of their electrochemical performance (Figure 14g). As proof-of-concept, a stretchable Li-air battery was integrated with wearable physiological devices to observe real-time bio-signals such as eye blinks, jaw clenches, and light muscle tension. Despite significant progress in stretchable metal-air batteries, novel materials and newly designed fabrication technology for stretchable metal-air batteries are urgently needed to realize reliable stretchable power source for wearable devices (Figure 14h). Table 2 shows a summary of recently reported performances of various stretchable batteries.

5. Summary and Perspective

The rapid development of stretchable energy-storage devices has opened new opportunities for wearable electronic devices. Among them, stretchable batteries that can store electrical energy through faradaic reactions have attracted extensive interest in the batteries and electronics research community because of their high energy density and good long-term stability. In this review, we have presented various stretchable batteries for wearable electronics. The development of reliable

stretchable batteries could be categorized as two main strategies of (i) stretchable materials and (ii) structural design.

We discussed electrode materials for stretchable batteries, including carbon-based materials (e.g., CNT and graphene), metal-based materials (e.g., Ag and Au), and hybrid nanocomposite-based materials (e.g., carbon-elastomeric polymer composites and metal-elastomeric polymer composites). Carbon-based materials with good electrochemical stability and mechanical robustness can serve as both anode materials and conductive fillers for fabricating a stretchable current collector. Also, carbon is a cost-effective material. Although carbon-based materials are indeed versatile materials in the stretchable batteries, their low electrical conductivity might limit the maintenance of electrical percolation under strain and the electrochemical performance of stretchable batteries. Metal-based materials with naturally high electrical conductivity can also be used as active materials, which can improve battery energy density and power density. However, during charging/discharging, unrestrained growth of metal dendrite could result in safety issue and severe degradation of the battery performance. Hybrid nanocomposite-based materials comprising conductive fillers and elastomers have become alternatives in the fabrication of stretchable electrodes with high stretchability and with high electrical durability under strain, but they have poor electrical properties. In addition, polymers are also used as

Table 2. Summary of the performances of recently reported stretchable batteries.

Battery type	Electrode layout	Stretchability [%]	Output voltage [V]	Capacity	Energy density	Cycle retention	Ref.
Zn–MnO ₂	Coplanar	100	1.3	3.5 mAh cm ⁻²	4.55 mWh cm ⁻²	–	[18a]
Zn–MnO ₂	Coplanar	100	1.5	3.87 mAh cm ⁻²	5.80 mWh cm ⁻²	–	[18b]
Zn–MnO ₂	Fiber-shape	300	1.48	302.1 mAh g ⁻¹	447 mWh g ⁻¹	98.5% after 500 cycles at 0% strain	[18n]
Zn–Ag	Coplanar	80	~1.62	0.19 mAh cm ⁻²	0.31 mWh cm ⁻²	80% after 1000 cycles at 80% strain	[40]
Zn–Ag	Coplanar	100	1.31	3 mAh cm ⁻²	3.93 mWh cm ⁻²	140% after 30 cycles at 100% strain	[73]
Zn–Ag	Serpentine	100	1.5	3.5 mAh cm ⁻²	5.25 mWh cm ⁻²	~100% after 20 cycles at 100% strain	[18j]
LIBs	Porous structure	80	1.75	120 mAh g ⁻¹	210 mWh g ⁻¹	70% after 300 cycles at 0% strain	[66]
LIBs	Origami	1300% linear deformable	2.65	0.2 mAh cm ⁻²	0.53 mWh cm ⁻²	–	[18e]
LIBs	Wavy layout	450	2.4	1.1 mAh cm ⁻²	2.64 mWh cm ⁻²	~85% after 100 cycles at 450% strain	[18f]
LIBs	Wavy layout	50	3.7	2.2 mAh cm ⁻²	8.14 mWh cm ⁻²	85% after 60 cycles at releasing state	[18k]
LIBs	Self-similar serpentine	300	2.2	1.1 mAh cm ⁻²	2.42 mWh cm ⁻²	~80% after 20 cycles at 0% strain	[18c]
LIBs	Fiber-shaped	600	2.2	91.3 mAh g ⁻¹	201 mWh g ⁻¹	90%, after 50 cycles at 100% strain	[86]
LIBs	Fiber-shaped	100	2.5	138 mAh g ⁻¹	345 mWh g ⁻¹	84% after 200 cycles at 100%	[18d]
LIBs	Fiber-shaped	100	2.5	92.4 mAh g ⁻¹	231 mWh g ⁻¹	92.1% after 100 cycles at 0% strain	[28]
ALBs	Coplanar	100	1.0	90 mAh g ⁻¹	90 mWh g ⁻¹	70% after 50 cycles at 100% strain	[18m]
ALBs	Sandwich	100	1.2	100 mAh g ⁻¹	120 mWh g ⁻¹	80% after 15 cycles at 100% strain	[53]
Li-air	Serpentine	100	2.7	7111 mAh g ⁻¹	2540 Wh kg ⁻¹	–	[85]
Al-air	Fiber-shaped	30	1.2	935 mAh g ⁻¹	1168 mWh g ⁻¹	–	[18i]
Na-ion battery	Porous structure	50	2.7	103 mAh g ⁻¹	278 mWh g ⁻¹	85% after 60 cycles at 50% strain	[18l]

materials for extensible batteries, but there are still issues such as low electrical conductivity.

Achieving safer batteries is an important consideration. To this end, the development of SPEs, GPEs, or stretchable separator membranes is required. In particular, GPEs with an ionic liquid are safe and have good ionic conductivity and mechanical strength, which are important in stretchable systems. Meanwhile, a stretchable separator membrane is also applicable to cells subjected to a high strain rate. However, because this topic has received little attention, various types of stretchable membranes with outstanding performance need to be developed using new materials and facile processes.

Although new materials and innovative breakthroughs for fabricating stretchable batteries have been demonstrated, some challenges remain for realizing reliable stretchable batteries, including (i) the degradation of electrochemical performance due to delamination and crack formation between the active materials and the stretchable substrate under strain, (ii) the design of electrodes that can maintain their electrical and mechanical properties even under arbitrary form such as biaxial/omnidirectional strains, and (iii) the development of interfacial materials with high stretchability and good electrochemical stability between electrodes.

To address the aforementioned issues, simple but straightforward strategies are needed. One of possible solutions for the delamination and crack formation is to utilize elastic binders that can accommodate high stress under arbitrary strain, while retaining desirable electrochemical performance. Another technical approach is to use a patterned current collector which can be fabricated by various methods such as a photolithographic process. This patterned structure would significantly improve the mechanical property of a current collector, and also strengthen the adhesion property between an active material and a current collector. Concerning interfacial materials, it is necessary to develop stretchable materials with high ionic conductivity and electrochemical stability. One way to obtain more outstanding materials would be to find new candidates by combining superior properties of each material, for example, combining more than two materials through copolymerization, chemical modifications, crosslinking each other and so on. Furthermore, packaging of the battery is one of the most important elements for stable cycle operation. Stretchable packaging materials should possess not only high stretchability, but also low air and water permeability. A common material for packaging is a silicone-based rubber and block-copolymer so far. However, these rubbers, which have loose polymer chains and low crystallinity, do not guarantee the battery performance. Intensive research, therefore, should be devoted to developing state-of-the-art materials with high mechanical elongation and low permeability simultaneously.^[87]

Apart from the material aspects, engineering of structures such as wavy structures, island-bridge structures, and origami/kirigami structures has been widely used as an effective strategy to manufacture stretchable batteries. Such structural engineering can ensure high stretchability and durability of device performance under strain through bonding of rigid materials (e.g., active materials) to compliant elastic materials

(e.g., PDMS and Ecoflex). However, the fabrication process of these configurations is relatively complex, leading to high manufacturing cost.

As demonstrations of stretchable batteries, various energy systems have been adopted as effective stretchable power supplies for wearable devices. However, the energy density and mechanical stretchability of these batteries are insufficient to satisfy the requirements of practical wearable devices. New conductive and active materials with outstanding characteristics, facile and cost-effective fabrication/assembly processes, and innovative concepts for structural configuration are needed to expedite the advance of reliable stretchable batteries for future wearable electronics.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: batteries • energy-storage devices • stretchable • structure design • wearable electronics

- [1] a) S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D.-H. Kim, *Adv. Mater.* **2016**, *28*, 4203–4218; b) S. I. Park, D. S. Brenner, G. Shin, C. D. Morgan, B. A. Copits, H. U. Chung, M. Y. Pullen, K. N. Noh, S. Davidson, S. J. Oh, *Nat. Biotechnol.* **2015**, *33*, 1280–1286.
- [2] I. You, B. Kim, J. Park, K. Koh, S. Shin, S. Jung, U. Jeong, *Adv. Mater.* **2016**, *28*, 6359–6364.
- [3] M. Ramuz, B. C. K. Tee, J. B. H. Tok, Z. Bao, *Adv. Mater.* **2012**, *24*, 3223–3227.
- [4] a) M. D. Dickey, *Adv. Mater.* **2017**, *29*, 1606425; b) D. Rus, M. T. Tolley, *Nature* **2018**, *521*, 467–475.
- [5] a) J. A. Rogers, T. Someya, Y. Huang, *Science* **2010**, *327*, 1603–1607; b) J. Kwon, Y. Takeda, R. Shiwaku, S. Tokito, K. Cho, S. Jung, *Nat. Commun.* **2019**, *10*, 54. c) I. You, M. Kong, U. Jeong, *Acc. Chem. Res.* **2018**, *52*, 63–72.
- [6] J. Y. Oh, S. Rondeau-Gagné, Y.-C. Chiu, A. Chortos, F. Lissel, G.-J. N. Wang, B. C. Schroeder, T. Kurosawa, J. Lopez, T. Katsumata, *Nature* **2016**, *539*, 411–415.
- [7] D.-H. Kim, J.-H. Ahn, W. M. Choi, H.-S. Kim, T.-H. Kim, J. Song, Y. Y. Huang, Z. Liu, C. Lu, J. A. Rogers, *Science* **2008**, *320*, 507–511.
- [8] N. Matsuhisa, M. Kaltenbrunner, T. Yokota, H. Jinno, K. Kuribara, T. Sekitani, T. Someya, *Nat. Commun.* **2015**, *6*, 7461.
- [9] F. Yi, H. Ren, J. Shan, X. Sun, D. Wei, Z. Liu, *Chem. Soc. Rev.* **2018**, *47*, 3152–3188.
- [10] a) C. Wang, C. Wang, Z. Huang, S. Xu, *Adv. Mater.* **2018**, *30*, 1801368; b) X. Chu, H. Zhang, H. Su, F. Liu, B. Gu, H. Huang, H. Zhang, W. Deng, X. Zheng, W. Yang, *Chem. Eng. J.* **2018**, *349*, 168–175; c) H. Zhang, H. Su, L. Zhang, B. Zhang, F. Chun, X. Chu, W. He, W. Yang, *J. Power Sources* **2016**, *331*, 332–339; d) H. Huang, H. Su, H. Zhang, L. Xu, X. Chu, C. Hu, H. Liu, N. Chen, F. Liu, W. Deng, *Adv. Electron. Mater.* **2018**, *4*, 1800179.
- [11] a) T. An, W. Cheng, *J. Mater. Chem. A* **2018**, *6*, 15478–15494; b) L. Li, Z. Lou, D. Chen, K. Jiang, W. Han, G. Shen, *Small* **2017**, *17*, 1702829.

- [12] a) Z. F. Liu, S. Fang, F. A. Moura, J. N. Ding, N. Jiang, J. Di, M. Zhang, X. Lepró, D. S. Galvão, C. S. Haines, N. Y. Yuan, S. G. Yin, D. W. Lee, *Science*. **2014**, *349*, 400–404; b) Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, *Nat. Commun.* **2015**, *6*, 10310; c) Z. Zhang, J. Deng, X. Li, Z. Yang, S. He, X. Chen, G. Guan, J. Ren, H. Peng, *Adv. Mater.* **2015**, *27*, 356–362; d) C. Choi, J. H. Kim, H. J. Sim, J. Di, R. H. Baughman, S. J. Kim, *Adv. Energy Mater.* **2016**, *16*, 1602021.
- [13] K. K. Fu, J. Cheng, T. Li, L. Hu, *ACS Energy Lett.* **2016**, *1*, 1065–1079.
- [14] a) M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, *104*, 4245–4269; b) P. Verma, P. Maire, P. Novák, *Electrochim. Acta* **2010**, *55*, 6332–6341; c) V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, *4*, 3243–3262; d) S.-Y. Lee, K.-H. Choi, W.-S. Choi, Y. H. Kwon, H.-R. Jung, H.-C. Shin, J. Y. Kim, *Energy Environ. Sci.* **2013**, *6*, 2414–2423.
- [15] a) P. G. Bruce, B. Scrosati, J.-M. Tarascon *Angew. Chem. Int. Ed.* **2008**, *47*, 2930–2946; *Angew. Chem.* **2008**, *120*, 2972–2989; b) C. Liu, F. Li, L.-P. Ma, H.-M. Cheng, *Adv. Mater.* **2010**, *22*, E28–E62.
- [16] a) C. Yan, P. S. Lee, *Small* **2014**, *10*, 3443–3460; b) W. Liu, M.-S. Song, B. Kong, Y. Cui, *Adv. Mater.* **2017**, *29*, 1603436; c) Z. Liu, F. Mo, H. Li, M. Zhu, Z. Wang, G. Liang, C. Zhi, *Small Methods* **2018**, *2*, 1800124.
- [17] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, G. M. Whitesides, *Nature* **1998**, *393*, 146–149.
- [18] a) M. Kaltenbrunner, G. Kettlgruber, C. Siket, R. Schwödauer, S. Bauer, *Adv. Mater.* **2010**, *22*, 2065–2067; b) A. M. Gaikwad, A. M. Zamarayeva, J. Rousseau, H. Chu, I. Derin, D. A. Steingart, *Adv. Mater.* **2012**, *24*, 5071–5076; c) S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, *Nat. Commun.* **2013**, *4*, 1543; d) J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang, X. Fang, W. Weng, Y. Wang, H. Peng, *Angew. Chem. Int. Ed.* **2014**, *53*, 7864–7869; *Angew. Chem.* **2014**, *126*, 7998–8003; e) Z. Song, T. Ma, R. Tang, Q. Cheng, X. Wang, D. Krishnaraju, R. Panat, C. K. Chan, H. Yu, H. Jiang, *Nat. Commun.* **2014**, *5*, 3140; f) W. Weng, Q. Sun, Y. Zhang, S. He, Q. Wu, J. Deng, X. Fang, G. Guan, J. Ren, H. Peng, *Adv. Mater.* **2015**, *27*, 1363–1369; g) Z. Song, X. Wang, C. Lv, Y. An, M. Liang, T. Ma, D. He, Y. J. Zheng, S. Q. Huang, H. Yu, *Sci. Rep.* **2015**, *5*, 10988.; h) Y. Sun, J. Lopez, H. W. Lee, N. Liu, G. Zheng, C. L. Wu, J. Sun, W. Liu, J. W. Chung, Z. Bao, *Adv. Mater.* **2016**, *28*, 2455–2461; i) Y. Xu, Y. Zhao, J. Ren, Y. Zhang, H. Peng, *Angew. Chem. Int. Ed.* **2016**, *55*, 7979–7982; *Angew. Chem.* **2016**, *128*, 8111–8114; j) A. M. Zamarayeva, A. E. Ostfeld, M. Wang, J. K. Duey, I. Deckman, B. P. Lechêne, G. Davies, D. A. Steingart, A. C. Arias, *Sci. Adv.* **2017**, *3*, 1602051; k) W. Liu, J. Chen, Z. Chen, K. Liu, G. Zhou, Y. Sun, M. S. Song, Z. Bao, Y. Cui, *Adv. Energy Mater.* **2017**, *7*, 1701076; l) H. Li, Y. Ding, H. Ha, Y. Shi, L. Peng, X. Zhang, C. J. Ellison, G. Yu, *Adv. Mater.* **2017**, *29*, 1700898; m) W.-J. Song, J. Park, D. H. Kim, S. Bae, M. J. Kwak, M. Shin, S. Kim, S. Choi, J. H. Jang, T. J. Shin, *Adv. Energy Mater.* **2018**, *8*, 1702478; n) H. Li, Z. Liu, G. Liang, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Tang, Y. Wang, *ACS Nano* **2018**, *12*, 3140–3148; o) K. Liu, B. Kong, W. Liu, Y. Sun, M. S. Song, J. Chen, Y. Liu, D. Lin, A. Pei, Y. Cui, *Joule* **2018**, *2*, 1857–1865.
- [19] K.-H. Choi, D. B. Ahn, S.-Y. Lee, *ACS Energy Lett.* **2018**, *3*, 220–236.
- [20] J. Ryu, T. Bok, S. Kim, S. Park, *ChemNanoMat* **2018**, *4*, 319–337.
- [21] T. Li, Z. Huang, Z. Suo, S. P. Lacour, S. Wagner, *Appl. Phys. Lett.* **2004**, *85*, 3435–3437.
- [22] a) D. Qi, Z. Liu, Y. Liu, W. R. Leow, B. Zhu, H. Yang, J. Yu, W. Wang, H. Wang, S. Yin, *Adv. Mater.* **2015**, *27*, 5559–5566; b) A. Zhou, R. Sim, Y. Luo, X. Gao, *J. Mater. Chem. A* **2017**, *5*, 21550–21559; c) P. Lee, J. Ham, J. Lee, S. Hong, S. Han, Y. D. Suh, S. E. Lee, J. Yeo, S. S. Lee, D. Lee, *Adv. Funct. Mater.* **2014**, *24*, 5671–5678.
- [23] a) M. Yu, B. S. Files, S. Areppalli, R. S. Ruoff, *Phys. Rev. Lett.* **2000**, *84*, 5552–5555; b) J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun’ko, *Carbon* **2006**, *44*, 1624–1652; c) J. P. Lu, *Phys. Rev. Lett.* **1997**, *79*, 1297–1300; d) Y. Zhai, Y. Dou, D. Zhao, P. F. Fulvio, R. T. Mayes, S. Dai, *Adv. Mater.* **2011**, *23*, 4828–4850.
- [24] a) C. Yu, C. Masarapu, J. Rong, B. Wei, H. Jiang, *Adv. Mater.* **2009**, *21*, 4793–4797; b) Z. Yu, X. Niu, Z. Liu, Q. Pei, *Adv. Mater.* **2011**, *23*, 3989–3994; c) M. S. Balogun, W. Qiu, F. Lyu, Y. Luo, H. Meng, J. Li, W. Mai, L. Mai, Y. Tong, *Nano Energy* **2016**, *26*, 446–455.
- [25] a) M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, A. J. Hart, *Science* **2013**, *339*, 535–540; b) W. Weng, Q. Sun, Y. Zhang, H. Lin, J. Ren, X. Lu, M. Wang, H. Peng, *Nano Lett.* **2014**, *14*, 3432–3438.
- [26] D.-Y. Cho, K. Eun, S.-H. Choa, H.-K. Kim, *Carbon* **2014**, *66*, 530–538.
- [27] a) S. Yao, Y. Zhu, *Adv. Mater.* **2015**, *27*, 1480–1511; b) S. Park, M. Vosguerichian, Z. Bao, *Nanoscale* **2013**, *5*, 1727–1752.
- [28] Y. Zhang, W. Bai, X. Cheng, J. Ren, W. Weng, P. Chen, X. Fang, Z. Zhang, H. Peng, *Angew. Chem. Int. Ed.* **2014**, *53*, 14564–14568; *Angew. Chem.* **2014**, *126*, 14792–14796.
- [29] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193–2203.
- [30] M. F. El-Kady, Y. Shao, R. B. Kaner, *Nat. Rev. Mater.* **2016**, *1*, 16033.
- [31] Q. Li, N. J. Bjerrum, *J. Power Sources* **2002**, *110*, 1–10.
- [32] S. Jin, Y. Jiang, H. Ji, Y. Yu, *Adv. Mater.* **2018**, *30*, 1802014.
- [33] a) B. Long, L. Luo, H. Yang, M. S. Balogun, S. Song, Y. Tong, *ChemistrySelect* **2018**, *3*, 6965–6971; b) B. Long, H. Yang, F. Wang, Y. Mao, M. S. Balogun, S. Song, Y. Tong, *Electrochim. Acta* **2018**, *284*, 271–278.
- [34] M. S. Balogun, Y. Zeng, W. Qiu, Y. Luo, A. Onasanya, T. K. Olaniyi, Y. Tong, *J. Mater. Chem. A* **2016**, *4*, 9844–9849.
- [35] a) J. Lee, J. Wu, M. Shi, J. Yoon, S.-I. Park, M. Li, Z. Liu, Y. Huang, J. A. Rogers, *Adv. Mater.* **2011**, *23*, 986–991; b) J. Xiao, A. Carlson, Z. J. Liu, Y. Huang, H. Jiang, J. A. Rogers, *Appl. Phys. Lett.* **2008**, *93*, 013109.
- [36] C. Wang, W. Zheng, Z. Yue, C. O. Too, G. G. Wallace, *Adv. Mater.* **2011**, *23*, 3580–3584.
- [37] a) D. Lin, Y. Liu, Y. Cui, *Nat. Nanotechnol.* **2017**, *12*, 194–206; b) X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, *Chem. Rev.* **2017**, *117*, 10403–10473.
- [38] E. T. Thostenson, Z. Ren, T.-W. Chou, *Compos. Sci. Technol.* **2001**, *61*, 1899–1912.
- [39] a) S. V. Ahir, Y. Y. Huang, E. M. Terentjev, *Polymer* **2008**, *49*, 3841–3854; b) Y. Y. Huang, E. M. Terentjev, *Polymer* **2012**, *4*, 275–295; c) A. V. Kyrylyuk, M. C. Hermant, T. Schilling, B. Klumperman, C. E. Koning, P. Van Der Schoot, *Nat. Nanotechnol.* **2011**, *6*, 364–369.
- [40] C. Yan, X. Wang, M. Cui, J. Wang, W. Kang, C. Y. Foo, P. S. Lee, *Adv. Energy Mater.* **2014**, *4*, 1301396.
- [41] L. V. Kayser, D. J. Lipomi, *Adv. Mater.* **2019**, *31*, 1806133.
- [42] S. Pang, Y. Gao, S. Choi, *Adv. Energy Mater.* **2018**, *8*, 1702261.
- [43] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, *Energy Environ. Sci.* **2014**, *7*, 3857–3886.
- [44] a) J.-C. Daigle, Y. Asakawa, A. Vijh, P. Hovington, M. Armand, K. Zaghib, *J. Power Sources* **2016**, *332*, 213–221; b) J. C. Jansen, K. Friess, G. Clarizia, J. Schauer, P. Izák, *Macromolecules* **2011**, *44*, 39–45; c) J. Y. Song, Y. Y. Wang, C. C. Wan, *J. Power Sources* **1999**, *77*, 183–197; d) H. B. Youcef, O. Garcia-Calvo, N. Lago, S. Devaraj, M. Armand, *Electrochim. Acta* **2016**, *220*, 587–594.
- [45] X. Yang, F. Zhang, L. Zhang, T. Zhang, Y. Huang, Y. Chen, *Adv. Funct. Mater.* **2013**, *23*, 3353–3360.
- [46] M. Kammoun, S. Berg, H. Ardebili, *J. Power Sources* **2016**, *332*, 406–412.
- [47] Y. Wang, B. Li, J. Ji, A. Eyler, W. H. Zhong, *Adv. Energy Mater.* **2013**, *3*, 1557–1562.
- [48] S. Choudhury, T. Saha, K. Naskar, M. Stamm, G. Heinrich, A. Das, *Polymer* **2017**, *112*, 447–456.
- [49] a) M. Egashira, H. Todo, N. Yoshimoto, M. Morita, *J. Power Sources* **2008**, *178*, 729–735; b) A. M. Stephan, K. S. Nahm, *Polymer* **2006**, *47*, 5952–5964.
- [50] J. Guan, Y. Li, J. Li, *Ind. Eng. Chem. Res.* **2017**, *56*, 12456–12463.
- [51] a) K.-H. Choi, S.-J. Cho, S.-H. Kim, Y. H. Kwon, J. Y. Kim, S.-Y. Lee, *Adv. Funct. Mater.* **2014**, *24*, 44–52; b) P. Hu, J. Choi, Y. Duan, Z. Liu, G. Cui, L. Chen, *J. Mater. Chem. A* **2016**, *4*, 10070–10083.
- [52] M. Xie, J. Wang, X. Wang, M. Yin, C. Wang, D. Chao, X. Liu, *Macromol. Res.* **2016**, *24*, 965–972.
- [53] M. Shin, W.-J. Song, H. Bin Son, S. Yoo, S. Kim, G. Song, N. S. Choi, S. Park, *Adv. Energy Mater.* **2018**, *8*, 1801025.
- [54] a) J. I. Kim, Y. Choi, K. Y. Chung, J. H. Park, *Adv. Funct. Mater.* **2017**, *27*, 1701768; b) S. Yoo, J.-H. Kim, M. Shin, H. Park, J.-H. Kim, S.-Y. Lee, S. Park, *Sci. Adv.* **2015**, *1*, 1500101.
- [55] a) B. Wang, S. Bao, S. Vinnikova, P. Ghanta, S. Wang, *NPJ Flex. Electron.* **2017**, *1*, 5; b) Y. Sun, W. M. Choi, H. Jiang, Y. Y. Huang, J. A. Rogers, *Nat. Nanotechnol.* **2006**, *1*, 201–207; c) D.-Y. Khang, J. A. Rogers, H. H. Lee, *Adv. Funct. Mater.* **2009**, *19*, 1526–1536; d) Y. Liu, M. Pharr, G. A. Salvatore, *ACS Nano* **2017**, *11*, 9614–9635.
- [56] D.-H. Kim, R. Ghaffari, N. Lu, J. A. Rogers, *Annu. Rev. Biomed. Eng.* **2012**, *14*, 113–128.
- [57] J.-H. Ahn, J. H. Je, *J. Phys. D: Appl. Phys.* **2012**, *45*, 103001.
- [58] D. Wirthl, R. Pichler, M. Drack, G. Kettlhuber, R. Moser, R. Gerstmayr, F. Hartmann, E. Bradt, R. Kaltseis, C. M. Siket, S. E. Schausberger, S. Hild, S. Bauer, M. Kaltenbrunner, *Sci. Adv.* **2017**, *3*, 1700053.
- [59] a) H. W. Kim, T. Y. Kim, H. K. Park, I. You, J. Kwak, J. C. Kim, H. Hwang, H. S. Kim, U. Jeong, *ACS Appl. Mater. Interfaces* **2018**, *10*, 40141–40148; b) Y. Zhang, S. Xu, H. Fu, J. Lee, J. Su, K. C. Hwang, J. A. Rogers, Y. Huang, *Soft Matter* **2013**, *9*, 8062–8070.
- [60] Y. Zhang, H. Fu, Y. Su, S. Xu, H. Cheng, J. A. Fan, K.-C. Hwang, J. A. Rogers, Y. Huang, *Acta Mater.* **2013**, *61*, 7816–7827.

- [61] S. Qu, Z. Song, J. Liu, Y. Li, Y. Kou, C. Ma, X. Han, Y. Deng, N. Zhao, W. Hu, *Nano Energy* **2017**, *39*, 101–110.
- [62] a) Q. Cheng, Z. Song, T. Ma, B. B. Smith, R. Tang, H. Yu, H. Jiang, C. K. Chan, *Nano Lett.* **2013**, *13*, 4969–4974; b) S. J. P. Callens, A. A. Zadpoor, *Mater. Today* **2018**, *21*, 241–264.
- [63] L. Xu, T. C. Shyu, N. A. Kotov, *ACS Nano* **2017**, *11*, 7587–7599.
- [64] a) W.-J. Song, S. Yoo, J.-I. Lee, J.-G. Han, Y. Son, S.-I. Kim, M. Shin, S. Choi, J.-H. Jang, J. Cho, *Chem. Asian J.* **2016**, *11*, 3382–3388; b) W.-J. Song, S. H. Joo, D. H. Kim, C. Hwang, G. Y. Jung, S. Bae, Y. Son, J. Cho, H. K. Song, S. K. Kwak, *Nano Energy* **2017**, *32*, 255–262; c) H. Son, M.-Y. Jeong, J.-G. Han, K. Kim, K. H. Kim, K.-M. Jeong, N.-S. Choi, *J. Power Sources* **2018**, *400*, 147–156.
- [65] a) C. Hwang, W.-J. Song, J.-G. Han, S. Bae, G. Song, N.-S. Choi, S. Park, H.-K. Song, *Adv. Mater.* **2018**, *30*, 1705445; b) T. Yoon, G. Song, A. M. Harzandi, M. Ha, S. Choi, S. Shadman, J. Ryu, T. Bok, S. Park, K. S. Kim, *J. Mater. Chem. A* **2018**, *6*, 15961–15967; c) C. Kim, G. Song, L. Luo, J. Y. Cheong, S.-H. Cho, D. Kwon, S. Choi, J.-W. Jung, C.-M. Wang, I.-D. Kim, *ACS Nano* **2018**, *12*, 8169–8176; d) S. Kalluri, M. Yoon, M. Jo, S. Park, S. Myeong, J. Kim, S. X. Dou, Z. Guo, J. Cho, *Adv. Energy Mater.* **2017**, *7*, 1601507; e) G. Song, J. Ryu, J. C. Kim, J. H. Lee, S. Kim, C. Wang, S. K. Kwak, S. Park, *Commun. Chem.* **2018**, *1*, 42; f) J.-G. Han, J. B. Lee, A. Cha, T. K. Lee, W. Cho, S. Chae, S. J. Kang, S. K. Kwak, J. Cho, S. Y. Hong, N.-S. Choi, *Energy Environ. Sci.* **2018**, *11*, 1552–1562.
- [66] W. Liu, Z. Chen, G. Zhou, Y. Sun, H. R. Lee, C. Liu, H. Yao, Z. Bao, Y. Cui, *Adv. Mater.* **2016**, *28*, 3578–3583.
- [67] a) K. Liu, Y. Liu, D. Lin, A. Pei, Y. Cui, *Sci. Adv. Mater.* **2018**, *4*, eaas9820; b) Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, C. Chen, *J. Power Sources* **2012**, *208*, 210–224; c) N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252–264; d) D. Larcher, J. M. Tarascon, *Nat. Chem.* **2015**, *7*, 19–29.
- [68] S. Gong, W. Cheng, *Adv. Energy Mater.* **2017**, *7*, 1700648.
- [69] a) D.-Y. Wang, C.-Y. Wei, M.-C. Lin, C.-J. Pan, H.-L. Chou, H.-A. Chen, M. Gong, Y. Wu, C. Yuan, M. Angell, *Nat. Commun.* **2017**, *8*, 14283; b) H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, *Energy Environ. Sci.* **2018**, *11*, 941–951; c) W. Zhang, J. Mao, S. Li, Z. Chen, Z. Guo, *J. Am. Chem. Soc.* **2017**, *139*, 3316–3319; d) H. Zhang, K. Ye, X. Huang, X. Wang, K. Cheng, X. Xiao, G. Wang, D. Cao, *J. Power Sources* **2017**, *338*, 136–144; e) C. Xia, J. Guo, Y. Lei, H. Liang, C. Zhao, H. N. Alshareef, *Adv. Mater.* **2018**, *30*, 1705580; f) M. Wang, C. Jiang, S. Zhang, X. Song, Y. Tang, H.-M. Cheng, *Nat. Chem.* **2018**, *10*, 667–672; g) W. Li, S. Hu, X. Luo, Z. Li, X. Sun, M. Li, F. Liu, Y. Yu, *Adv. Mater.* **2017**, *29*, 1605820.
- [70] R. K. Guduru, J. C. Icaza, *Nanomaterials* **2016**, *6*, 41.
- [71] a) D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah, L. F. Nazar, *Nat. Energy* **2016**, *1*, 16119; b) R. Trócoli, F. La Mantia, *ChemSusChem* **2015**, *8*, 481–485; c) M. Song, H. Tan, D. Chao, H. J. Fan, *Adv. Funct. Mater.* **2018**, *28*, 1802564; d) N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, *Nat. Commun.* **2017**, *8*, 405; e) P. Gu, M. Zheng, Q. Zhao, X. Xiao, H. Xue, H. Pang, *J. Mater. Chem. A* **2017**, *5*, 7651–7666; f) J. F. Parker, C. N. Chervin, I. R. Pala, M. Machler, M. F. Burz, J. W. Long, D. R. Rolison, *Science* **2017**, *356*, 415–418.
- [72] G. Kettlergruber, M. Kaltenbrunner, C. M. Siket, R. Moser, I. M. Graz, R. Schwödauer, S. Bauer, *J. Mater. Chem. A* **2013**, *1*, 5505–5508.
- [73] R. Kumar, J. Shin, L. Yin, J. M. You, Y. S. Meng, J. Wang, *Adv. Energy Mater.* **2017**, *7*, 1602096.
- [74] a) A. Konarov, N. Voronina, J. H. Jo, Z. Bakenov, Y.-K. Sun, S.-T. Myung, *ACS Energy Lett.* **2018**, *3*, 2620–2640; b) A. R. Mainar, E. Iruin, L. C. Colmenares, A. Kvasha, I. de Meatz, M. Bengoechea, O. Leonet, I. Boyano, Z. Zhang, J. A. Blazquez, *J. Energy Storage* **2018**, *15*, 304–328; c) Y. Li, J. Fu, C. Zhong, T. Wu, Z. Chen, W. Hu, K. Amine, J. Lu, *Adv. Energy Mater.* **2018**, *8*, 1802605.
- [75] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938–943.
- [76] P. Hu, M. Yan, T. Zhu, X. Wang, X. Wei, J. Li, L. Zhou, Z. Li, L. Chen, L. Mai, *ACS Appl. Mater. Interfaces* **2017**, *9*, 42717–42722.
- [77] S. Higashi, S. W. Lee, J. S. Lee, K. Takechi, Y. Cui, *Nat. Commun.* **2016**, *7*, 11801.
- [78] W. Li, K. Wang, M. Zhou, H. Zhan, S. Cheng, K. Jiang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 22059–22066.
- [79] a) Y. Li, H. Dai, *Chem. Soc. Rev.* **2014**, *43*, 5257–5275; b) M. A. Rahman, X. Wang, C. Wen, *J. Electrochem. Soc.* **2013**, *160*, A1759–A1771; c) J.-S. Lee, S. T. Kim, R. Cao, N.-S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34–50.
- [80] F. Cheng, J. Chen, *Chem. Soc. Rev.* **2012**, *41*, 2172–2192.
- [81] J. Park, M. Park, G. Nam, J.-S. Lee, J. Cho, *Adv. Mater.* **2015**, *27*, 1396–1401.
- [82] a) S. T. Senthilkumar, Y. Wang, H. Huang, *J. Mater. Chem. A* **2015**, *3*, 20863–20879; b) R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, D. Aurbach, *Adv. Mater.* **2011**, *23*, 5641–5644.
- [83] W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang, X. M. Tao, *Adv. Mater.* **2014**, *26*, 5310–5336.
- [84] Y. Xu, Y. Zhang, Z. Guo, J. Ren, Y. Wang, H. Peng, *Angew. Chem. Int. Ed.* **2015**, *54*, 15390–15394; *Angew. Chem.* **2015**, *127*, 15610–15614.
- [85] L. Wang, Y. Zhang, J. Pan, H. Peng, *J. Mater. Chem. A* **2016**, *4*, 13419–13424.
- [86] Y. Zhang, W. Bai, J. Ren, W. Weng, H. Lin, Z. Zhang, H. Peng, *J. Mater. Chem. A* **2014**, *2*, 11054–11059.
- [87] W. Song, S. Lee, G. Song, S. Park, *ACS Energy Lett.* **2018**, *4*, 177–186.

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