



Flexible 1D Batteries: Recent Progress and Prospects

Yun-Hai Zhu, Xiao-Yang Yang, Tong Liu, and Xin-Bo Zhang*

With the rapid development of wearable and portable electronics, flexible and stretchable energy storage devices to power them are rapidly emerging. Among numerous flexible energy storage technologies, flexible batteries are considered as the most favorable candidate due to their high energy density and long cycle life. In particular, flexible 1D batteries with the unique advantages of miniaturization, adaptability, and weavability are expected to be a part of such applications. The development of 1D batteries, including lithium-ion batteries, zinc-ion batteries, zinc–air batteries, and lithium–air batteries, is comprehensively summarized, with particular emphasis on electrode preparation, battery design, and battery properties. In addition, the remaining challenges to the commercialization of current 1D batteries and prospective opportunities in the field are discussed.

1. Introduction

Flexible and wearable electronics, such as Apple smart watches, Google Glass, Samsung Galaxy Fold, Huawei Mate X, presented a prominent technological trend for future lifestyles have attracted considerable attention in recent years.^[1–5] Benefiting from their unique features in terms of mechanical flexibility, high portability, and lightweight, the flexible/wearable electronics not only change the conventional consumer electronics but also bring many new areas such as artificial skins, implantable medical devices and epidermal sensors into social life.^[6–9] As the commercially available power devices are typically bulk and rigid, which cannot satisfy the standards of flexible/wearable electronics that require portability and flexibility, developing reliable power sources with high flexibility and stretchability are urgently needed.^[10–12]

Y.-H. Zhu, X.-Y. Yang, T. Liu, Prof. X.-B. Zhang
State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022, China
E-mail: xbzhang@ciac.ac.cn

Y.-H. Zhu, X.-Y. Yang
Key Laboratory of Automobile Materials (Jilin University)
Ministry of Education
Department of Materials Science and Engineering
Jilin University
Changchun 130022, China

T. Liu, Prof. X.-B. Zhang
University of Science and Technology of China
Hefei 230026, Anhui, China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201901961>.

DOI: 10.1002/adma.201901961

Among various flexible energy storage devices, flexible batteries are considered as the most promising candidates to power the future flexible/wearable electronics due to their relatively high energy density and long cycle life.^[13–16] Recently, numerous flexible batteries have already been demonstrated successfully, while most of them are fabricated in a planar architecture with large structure and limited flexibility, far away from the requirements of flexible/wearable electronic devices.^[17–20] Compared with the traditional planar structure, the 1D shape possesses much prominent superiority, such as miniaturization, adaptability, and weavability, which make it more attractive for flexible/wearable electronics.^[21–25]

In this review, from the viewpoint of electrode preparations, battery designs, and battery electrochemical and mechanical properties, recent progress of flexible 1D batteries has been summarized, focusing on Li-ion batteries (LIBs), Zn-ion batteries (ZIBs), Zn–air batteries (ZABs), and Li–air batteries (LABs). In the first section, flexible 1D LIBs with the different configurations including coaxial, twisted, and stretchable structures are presented. In the next section, 1D ZIBs are introduced detailedly from the standpoint of the anode types. Following the sections, special requirements for air cathode, electrolyte and metal anode in metal–air batteries have been highlighted from the perspective of designing flexible 1D battery. In addition, some successful demonstrations of fabric batteries composed of 1D batteries have been described. In the end, we also discuss the existing challenges and future directions of 1D batteries to provide some valuable insights into its practical applications.

2. Flexible 1D Lithium-Ion Batteries

Rechargeable LIBs possesses high energy and power densities, as well as longevity, which are expected to contribute to the flexible/wearable electronic devices.^[26–28] Up to now, a number of 1D LIBs with small, light, flexible designs have been promulgated which can be deformed into any shapes even woven into textiles. Per the relative position of the two electrodes, the configurations of 1D LIBs can be divided into coaxial and twisted structure.^[21,29] In a typical coaxial structure, the flexible outer electrode is wound around the inner electrode with a separator between them, forming a core–shell architecture (Figure 1a). In a twisted structure, two fiber electrodes are intertwined together at a certain twisting angle to form a double-helix structure (Figure 1b). When the twisting angle is zero, the two fibers are in a parallel arrangement. Additionally, to enhance

the stretchability of 1D devices, a stretchable structure has also been established by coiling the fiber electrodes along an elastic substrate, as illustrated in Figure 1c.^[29]

2.1. Coaxial Structure Lithium-Ion Batteries

As a primitive concept for battery model, cable-type LIBs might provide the necessary breakthrough in wearable electronics due to their excellent mechanical flexibility. Recently, Kwon et al. first demonstrated a flexible cable-type LIB, which composed of hollow spiral Ni/Sn anode, LiCoO₂ tubular cathode, modified polyethylene terephthalate membrane, and the shrunken packaging insulator, as illustrated in Figure 2a.^[30] Therein, the spring structure of Ni/Sn anode with improved electrolyte permeability could enhance battery performance. As a result, this flexible LIB showed a high specific capacity of 1.0 mAh cm⁻¹ with the voltage plateau at ≈3.5 V. Additionally, this cable-type LIB was highly flexible and mechanically stable. As shown in Figure 2b, the voltage of the battery remained stable as the battery was bent to different states. Even more, red light-emitting diode (LED) screen was also successfully operated by the cable-type LIB under severely twisting and knotting (Figure 2c,d).

Although, metal substrates possess high electrical conductivity and mechanical strength, the direct use of them in flexible and wearable device is impeded by their heavy and rigid nature. Compared with metal substrates, carbon current collectors are characterized with ultralight weight and high flexibility, which are more favorable for flexible 1D LIB. To this end, Weng et al. fabricated fiber electrodes by using aligned carbon nanotube (CNT) as flexible substrates to deposit Si and lithium manganate (LMO), respectively.^[31] Afterward, a coaxial fiber-shaped LIB with a diameter of 2 mm was achieved by sequentially winding CNT/Si and CNT/LMO hybrid fibers onto a cotton fiber, as shown in Figure 2e. Owing to the high stability of the CNT/Si and CNT/LMO fiber electrodes, this fiber-shaped LIB exhibited high specific capacity of 106.5 mAh g⁻¹ at the first cycle and maintained 87% of the original capacity even after 100 cycles (Figure 2f). Moreover, the fiber-shaped LIB had been further demonstrated to lighten up an LED (Figure 2g), meaning its reliable application. Subsequently, Wu et al. employed CNT woven microfilms (CMFs) as current collectors to fabricate flexible 1D LIBs.^[32] Previously, the LiCoO₂ (LCO) and Li₄Ti₅O₁₂ (LTO) were coated on CMFs as cathode (LCO/CMF) and anode (LTO/CMF), respectively. Owing to the roughened surfaces and nanoporous architectures of CMFs,

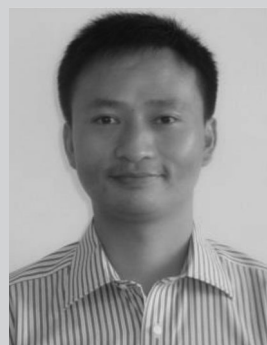


Yun-Hai Zhu received his B.S. degree in materials science and engineering from Hubei University in 2014. He is currently pursuing a Ph.D. in materials science at Jilin University of China. His current interests include design and synthesis of functional materials for sodium/potassium ion batteries and flexible energy storage devices.



Xiao-Yang Yang received his B.S. degree in materials science and engineering from Shandong University of Technology in 2014. He is currently pursuing a Ph.D. in materials science at Jilin University of China. His current research interests include the synthesis and characterization of efficient energy storage

materials in lithium–air batteries and flexible energy storage devices.



Xin-Bo Zhang is a full professor at Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences (CAS). He obtained his Ph.D. degree in inorganic chemistry from CIAC. His interests mainly focus on functional inorganic materials for batteries, fuel cells, and electrochemical catalysis.

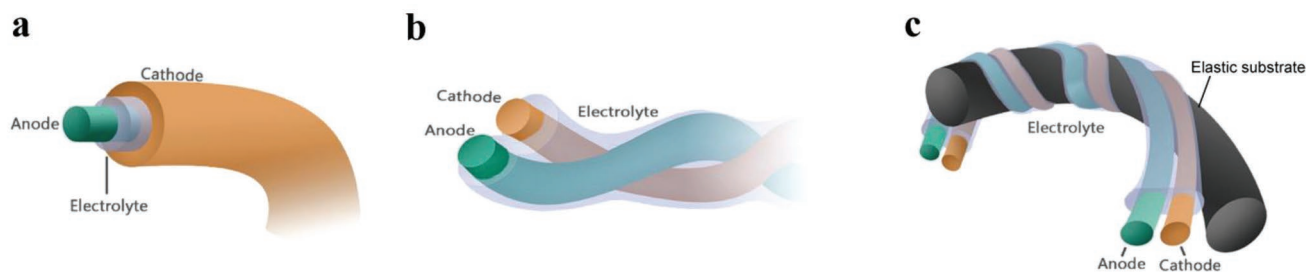


Figure 1. a–c) Schematic illustration of coaxial (a), twisted (b), and stretchable (c) 1D LIBs. a–c) Reproduced with permission.^[29] Copyright 2018, the Royal Society of Chemistry.

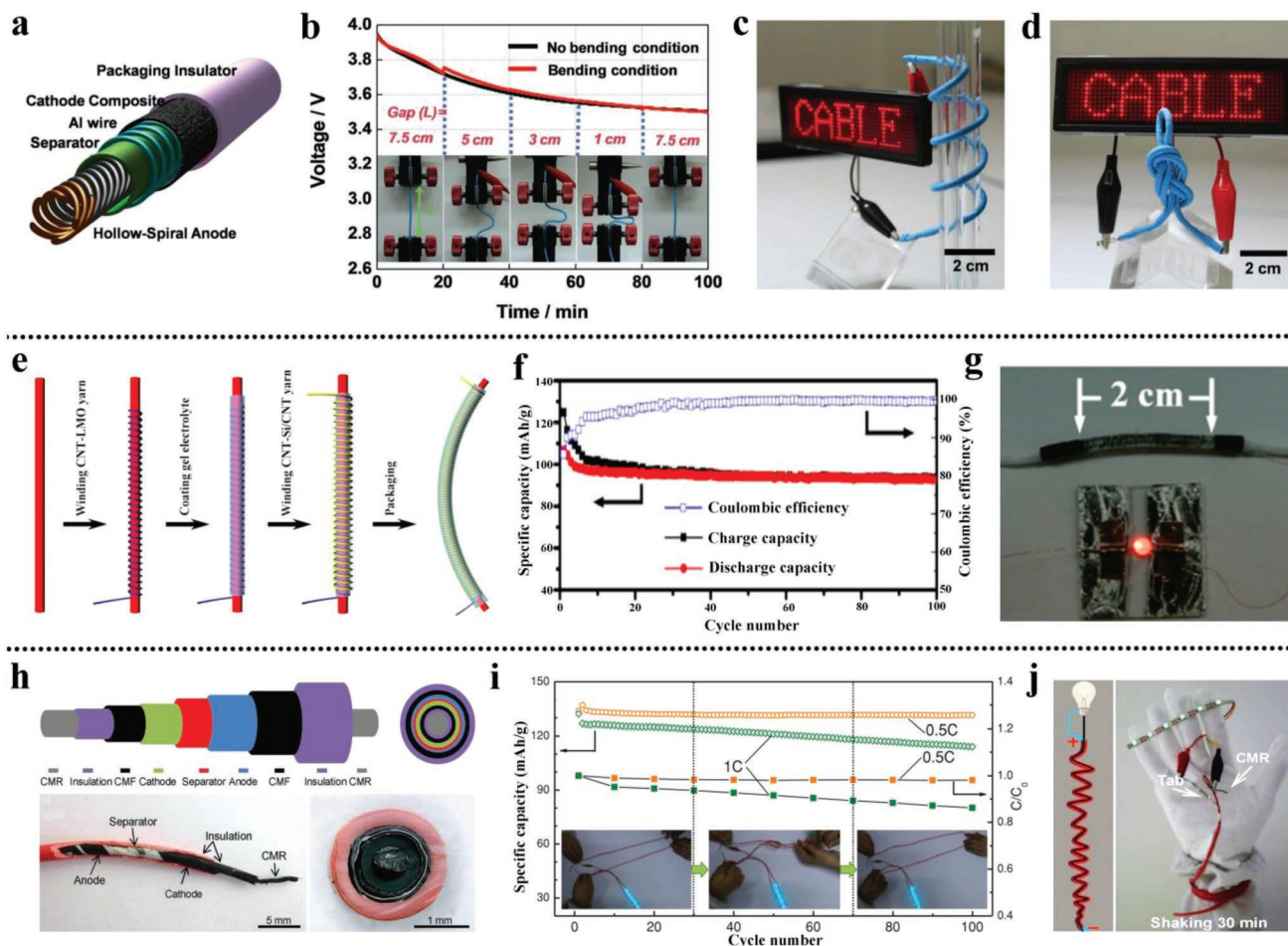


Figure 2. a) Schematic diagram of the cable-type LIB. b) Discharge characteristics with variation in bending strain. c,d) Photographs of the cable-type LIB under various bending conditions powering a red LED screen. a–d) Reproduced with permission.^[30] Copyright 2012, Wiley-VCH. e) Schematic illustration of the fabrication of the coaxial fiber full LIB. f) Long-life performance of the fiber-shaped LIB. g) Photograph of a fiber-shaped LIB powering an LED. e–g) Reproduced with permission.^[31] Copyright 2014, American Chemical Society. h) Schematic diagram and prototype of the cable-type LIB. i) Cycling performance and the dependence of specific capacity on the number of cycle times of the device between releasing and twisting states. j) A demonstration of the operation, flexibility, and weavability of the cable-type LIB. h–j) Reproduced with permission.^[32] Copyright 2018, Wiley-VCH.

both cathode and anode possessed an ultrahigh-tap density. The prototype and structure this flexible 1D LIB was shown in Figure 2h, which composed of CNT macropore (CMR), LCO/CMF, separator, LTO/CMF, and insulating layer. Notably, this 1D LIB exhibited extremely high volume energy density of 215 mWh cm^{-3} because of the both electrodes with ultrahigh-tap density. Additionally, the performance of this 1D LIB was quite insensitive to the deformation process (Figure 2i,j), demonstrating the excellent flexibility and stability of the battery at operation state.

2.2. Twisted Structure Lithium-Ion Batteries

Compared with coaxial structure LIBs, the LIBs with twisted structure are always smaller, lighter, and more flexible, making them more suitable for flexible/wearable electronics that required miniaturization, adaptability, and weavability. Until now, several works on twisted structure LIBs have been successfully

demonstrated. For instance, Ren et al. fabricated a fiber-shaped LIB with high performance by intertwining a Li wire and a CNT/MnO₂ hybrid fiber (Figure 3a) closely together.^[33] The CNT/MnO₂ hybrid fiber was first fabricated by depositing MnO₂ on the CNT. Owing to high electrochemical active of MnO₂ and the high electrical conductivity of CNT fiber, this twisted LIB delivered a high capacity of $109.6 \text{ mAh cm}^{-3}$. Subsequently, Lin et al. fabricated another twisted battery consisted of a CNT/Si hybrid fiber and a Li wire (Figure 3b).^[34] This CNT/Si composite fiber was synthesized via depositing nanometer Si onto aligned CNT film by an electron-beam evaporation technique. As a result, amorphous Si was uniformly coated on the surface of CNT. Benefitting from the high specific capacity of amorphous Si and high mechanical strength of CNT, this fiber-shaped battery delivered high reversible capacities of 1670 mAh g^{-1} and excellent mechanical stability with the capacity almost unchanged even after being bended for 100 cycles.

Unfortunately, the utilization of Li metal may produce safety risk, significantly impeded the practical applications of the

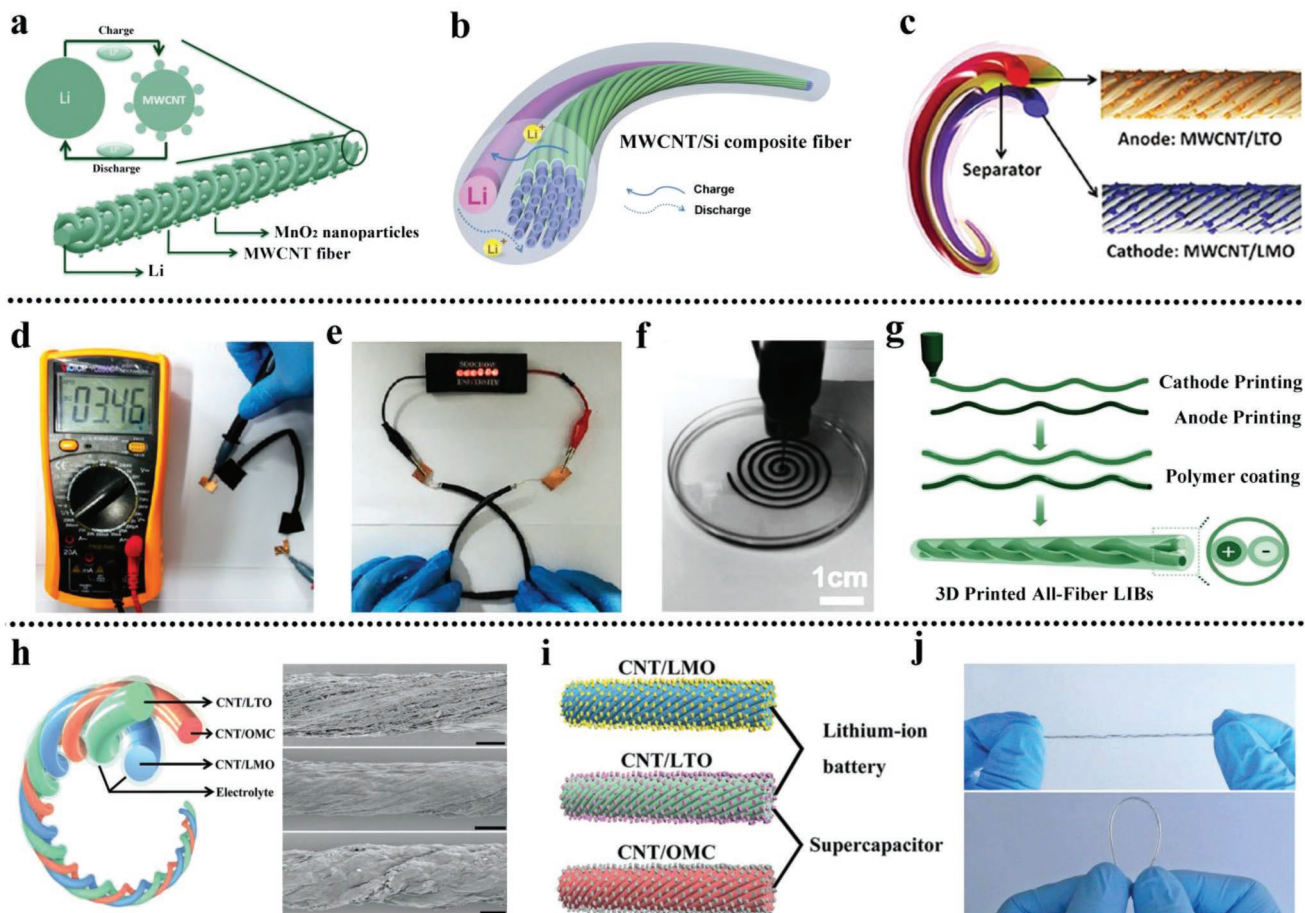


Figure 3. a) Schematic illustration of the fiber-shaped LIB composed of an MWCNT/MnO₂ composite fiber and a Li wire. Reproduced with permission.^[33] Copyright 2013, Wiley-VCH. b) Schematic illustration of the fiber-shaped LIB composed of an MWCNT/Si composite fiber and a Li wire. Reproduced with permission.^[34] Copyright 2014, Wiley-VCH. c) Schematic illustration of the fiber-shaped LIB composed of an MWCNT/LTO composite fiber and an MWCNT/LMO composite fiber. Reproduced with permission.^[37] Copyright 2014, Wiley-VCH. d,e) Demonstration of the flexibility of the full titania/LiMn₂O₄ fiber battery. d,e) Reproduced with permission.^[38] Copyright 2017, American Chemical Society. f,g) The printing process of 3D fiber electrodes (f) and the fabrication process of 3D-printed all-fiber flexible LIBs (g). f,g) Reproduced with permission.^[43] Copyright 2017, Wiley-VCH. h,i) Schematic illustration of the structure of a fiber-shaped hybrid energy storage device. j) Photographs of the fiber-shaped LIB being deformed into different shapes. h–j) Reproduced with permission.^[44] Copyright 2015, Wiley-VCH.

above 1D LIBs. To this end, an alternative is highly desired to replace Li metal wire with other novel fiber electrodes. Spinel LTO, a zero-strain insertion material, is supposed to be a promising anode due to its relatively high lithiation potential (1.54 vs Li/Li⁺) avoided the formation of dendritic lithium.^[35,36] Recently, Ren et al. designed a fiber-shaped full LIB by using CNT/LMO composite fiber as cathode and CNT/LTO composite fiber as anode.^[37] As shown in Figure 3c, the two fibers separated by a poly(vinylidene fluoride) (PVDF) separator were encapsulated into a heat-shrinkable tube, forming a fiber-shaped full LIB. The obtained fiber-shaped LIB exhibited superior electrochemical properties, including high energy densities of 27 Wh kg⁻¹ (17.7 mWh cm⁻³) and high power densities of 880 W kg⁻¹ (0.56 W cm⁻³), which were an order of magnitude higher than the densities of the reported 2D LIB. Additionally, the fiber-shaped LIBs were mechanically flexible and could withstand various deformations without being destroyed.

Titanium dioxide is another promising anode material for LIBs due its nontoxicity, safety, and excellent capacity retention.

To this end, Geng and co-workers designed a novel titania/reduced graphene oxide (rGO) composites fiber for using in 1D full LIB.^[38] This titania/rGO fiber was composed of titania and rGO sheets stacked regularly, exhibiting high linear density, mechanical strength, and electrical conductivity. As a result, a fiber-shaped full LIB with titania/rGO fiber as anode and LMO fiber as cathode exhibited excellent mechanical flexibility and superior battery performances (Figure 3d,e).

Up to now, the most reported fiber electrodes are heterogeneous complexes with active materials coated on flexible substrates. Owing to the low active materials loading and the unstable interface among the components, this heterogeneous structure may causes undesirable consequences in 1D battery, such less flexibility, low energy density, and inferior cycle life.

3D printing, the most advanced additive manufacturing technologies, has brought a global manufacturing revolution due to its high manufacturing efficiency, scalability, and economically.^[39,40] Among them, 3D extrusion-based printing method,^[41,42] the most common and probably the simplest 3D

printing technique, is expected to produce homogeneous fiber electrodes in a fast and scalable way. Recently, for the first time, Wang et al. fabricated fiber electrodes for using in flexible 1D LIB by this method.^[43] To prepare fiber electrodes, the anode/cathode inks were first obtained by mixing CNTs with LTO and lithium iron phosphate (LFP), respectively. After that, the ink materials were extruded from the 3D printing syringe into ethanol solution, forming smooth long fiber electrodes with excellent flexibility and high mechanical strength (Figure 3f). More encouragingly, an all-fiber quasi-solid-state LIB was successfully fabricated by twisting the printed cathode and anode fibers together with gel polymer electrolyte (GPE) as quasi-solid electrolyte (Figure 3g). This fiber-shaped LIB exhibited high capacity (110 mAh g^{-1}) and superior flexibility, demonstrating its potential application in future flexible/wearable devices.

LIB shows high energy density but low power density, while the supercapacitor displays the opposite performance. Up to now, it remains great challenging to simultaneously achieve high energy and power density in one energy storage device. To overcome this limitation, Zhang et al. produced a flexible 1D hybrid energy storage device that could function as both LIB and supercapacitor.^[44] As shown in Figure 3h, three fibers including aligned CNT/LMO, aligned CNT/LTO, and aligned CNT/ordered mesoporous carbon fiber were first coated with GPE, followed by being twisted together to form a hybrid device. When the aligned CNT/LMO and aligned CNT/LTO fibers were

connected, a battery with high energy density of 90 Wh kg^{-1} was produced. When the aligned CNT/ordered mesoporous carbon (OMC) and aligned CNT/LTO fibers were connected; a supercapacitor with high-power density of 5970 W kg^{-1} was generated (Figure 3i). Notably, this supercapacitor component could be self-charged by the LIB. In addition, this hybrid device is highly flexible and could bear various deformations (Figure 3j), displaying its promising prospect as a flexible power source.

2.3. Stretchable Lithium-Ion Batteries

The above flexible 1D LIBs could withstand various deformations including bending, folding, twisting, and knotting, while their structure is inevitably destroyed under stretching conditions that required in the real wearable electronic devices. Therefore, it is unavoidable to develop the stretchable LIBs that could be deformed along with the dynamic motions of the wearable electronics.^[15] Generally, the primary strategy to fabricate stretchable fiber-shaped LIBs was to design battery on the elastic substrate. Recently, Zhang et al. created a superstretchy LIB on polydimethylsiloxane (PDMS) elastic fiber.^[45] As illustrated in Figure 4a, the CNT/LMO and CNT/LTO composite fibers were first produced by the “suspension–deposition–scrolling” method, serving as the cathode and anode, respectively. Subsequently, the two fibers were parallelly wound onto a PDMS

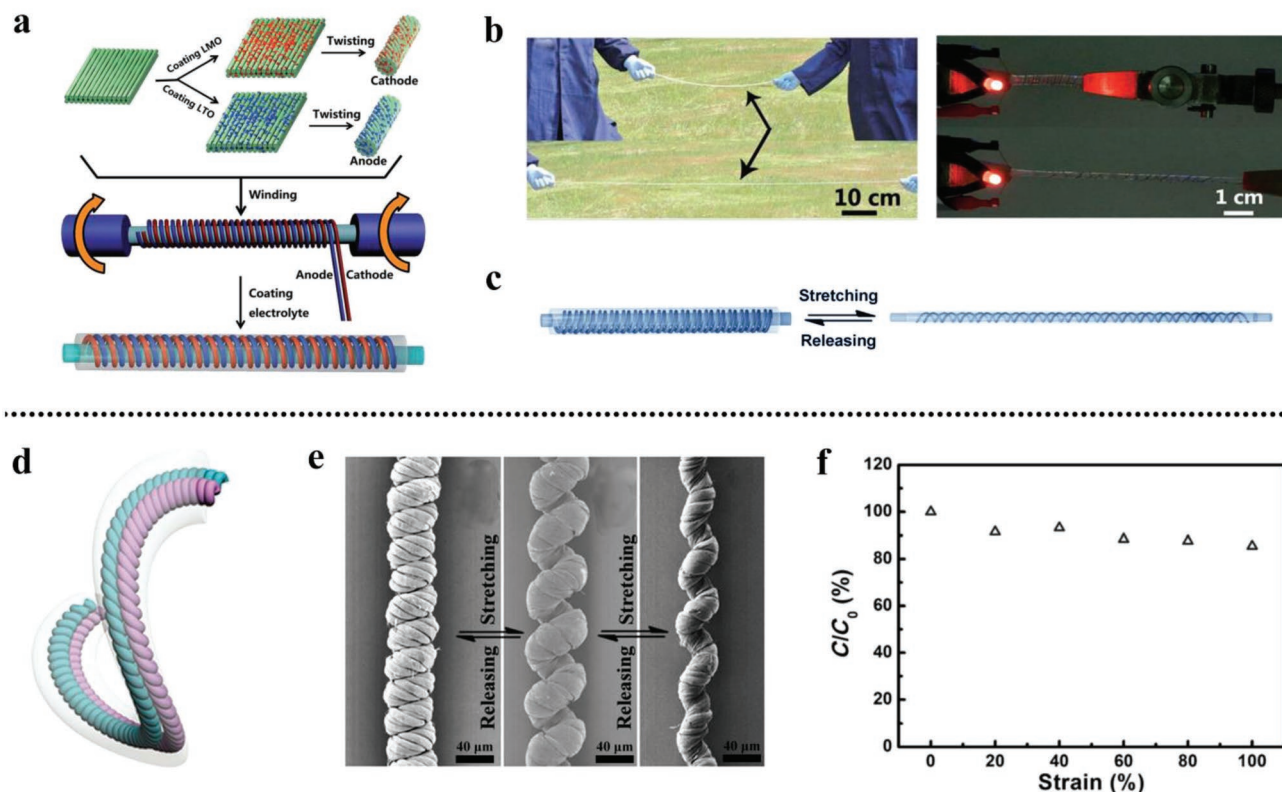


Figure 4. a) Schematic illustration of the fabrication of the superstretchy LIB based on an MWCNT/LMO composite fiber and an MWCNT/LTO composite fiber. b,c) Photograph (b) and the schematic illustration (c) of a stretchable fiber-shaped battery under stretching conditions. b,c) Reproduced with permission.^[45] Copyright 2014, the Royal Society of Chemistry. d) Schematic illustration of the spring-like stretchable LIB. e) SEM images of a fiber at different strains. f) Evolution of specific capacitance with strain. d–f) Reproduced with permission.^[46] Copyright 2014, Wiley-VCH.

elastic fiber. Finally, a superstretchy LIB was fabricated after coating with GPE and PDMS membrane. Owing to the ingenious design, this fiber-shaped battery showed highly stretchable property (Figure 4b) and excellent electrochemical stability, retaining up to 88% of the initial capacity even after stretching by 600%. Notably, the stretchability of this fiber-shaped LIB was derived from the PDMS elastic matrix and the double-helix structure of fiber electrodes. Upon stretching, the pitch length between two fibers increased as the PDMS substrate stretching, remaining the double-helix structure unchanged (Figure 4c). Upon releasing, the structure of this battery recovered to its original state.

Although, the introduction of elastic polymer substrates makes the 1D LIBs more suitable to the notion of flexible/wearable electronics; it inevitably increases the volume and weight of the battery, leading to a low specific capacitance and energy density. In addition, these elastic polymer substrates usually have low operating temperature and poor mechanical properties, making them unstable when applying in flexible/wearable electronics. To avoid the use of noncapacitive elastic substrates, a novel and effective strategy for achieving stretchable fiber-shaped LIBs has been presented by employing spring-like fiber electrodes (Figure 4d).^[46] Specifically, several aligned CNT fibers were first over-twisted together to fabricate the spring-like fiber. This spring-like fiber with superhigh stretchability could bear stretching strain over 300% through the change of its own spring-like structure (Figure 4e). Subsequently, LMO and LTO nanoparticles were loaded on two spring-like fibers, serving as cathode and anode, respectively. After that, an elastic fiber-shaped LIB was successfully fabricated by twisting the as-prepared two electrodes together. Thanks to the novel stretchability originated from spring-like structure, the elastic fiber-shaped LIBs showed high stretchability and stable performance, maintaining 85% of the initial capacity under a large strain of 100% (Figure 4f). Furthermore, this fiber-shaped LIB exhibited a linear specific capacity enhanced by 600% since no noncapacitive elastomeric polymers were used, making it more adaptable for flexible/wearable electronics.

Similar to LIBs, other alkaline-ion batteries, including sodium-ion batteries^[47,48] and potassium-ion batteries,^[49,50] show an operation mechanism in a rocking-chair fashion. Fortunately, owing to the abundant resource of raw material, sodium-ion batteries and potassium-ion batteries are always with low cost, which are expected to be applied to flexible electronic devices if the energy density is not the main factor.

3. Flexible 1D Zinc-Ion Batteries

Owing to the advantages of low-cost, high operational safety, and environmental benignity, aqueous rechargeable batteries have received increasing attention as one of the most promising energy storage system for flexible/wearable electronics.^[51–53] Furthermore, aqueous rechargeable batteries usually have higher power densities due to the higher ionic conductivities of the aqueous electrolytes compared to that of nonaqueous electrolytes. Among the various aqueous rechargeable batteries, aqueous ZIBs are regarded as the most favorable candidate as

the Zn anode possesses low redox potential, high theoretical capacity, and excellent stability in water.^[54–56] As a result, 1D ZIBs have been widely investigated and expected to power the next-generation flexible/wearable electronics.

3.1. Flexible 1D Zinc-Ion Batteries with Metal Anodes

Manganese dioxides (MnO_2) with tunnel or layered structure allowing reversible insertion/extraction of Zn^{2+} ions has gained increasing attention in 1D ZIBs due to their unique advantages, such as low-cost, abundant reserves, environmental friendliness, low toxicity, and multiple valence states.^[57–59] To this end, Wang et al. created a flexible cable-type ZIB by using MnO_2 @CNT fiber as the cathode.^[60] As shown in Figure 5a, the MnO_2 @CNT fiber was first produced by an easy electrochemical deposition process. Subsequently, it laminated together with separator and Zn wire in turn, followed by being encapsulated in a heat-shrinkable tube to form a flexible cable-type ZIB with a high energy density of 437 Wh kg^{-1} . This obtained cable-type ZIB exhibited superior flexibility and excellent electrochemical stability, which could be folded into spiral shape (Figure 5b) and bended over 100 cycles without influencing its electrochemical performance (Figure 5c).

Traditional ZIBs always employ a typical mechanism with the insertion/extraction of Zn ion. Recently, Wan et al. developed a cable-type flexible Zn–organic battery with dual-ion hybrid mechanism.^[61] Although, the structure of this cable-type battery is similar with that of other reported 1D batteries (Figure 5d), its working mechanism is totally different from traditional ion batteries. In this cable-type Zn/polyaniline battery, two types of carriers (CF_3SO_3^- and Zn^{2+}) simultaneously shuttled between the cathode and anode, achieving a reversible capacity of 106 mAh g^{-1} . Additionally, this cable-type Zn/polyaniline battery was flexible as it powers an LED array under bending states (Figure 5e), paving the way for the advanced applications of ZIBs in the field of flexible/wearable electronics.

Although much effort has been made to flexibilize batteries, current flexible batteries are still quite fragile, demonstrating very poor recuperability after severe deformation. To this end, Wang et al. designed a smart wire-shaped flexible ZIB with a function of shape memory.^[62] The structure of the smart wire-shaped ZIB was illustrated in Figure 5f, which mainly contained of a MnO_2 /PPy@SS cathode (PPy-coated MnO_2 on stainless steel yarn), a Zn@NT anode (Zn on Nitinol wire), and the gelatin–borax GPE. As an energy storage device, this wire-shaped ZIB delivered a high discharge capacity of 174.2 mAh g^{-1} and a stable cycle performance above 1000 cycles. Impressively, because of the intriguing shape memory effect and pseudoelasticity of Nitinol wire, this smart battery could recover from deformation effectively. As shown in Figure 5g, this wire-shaped battery recovered to its original shape after being immersed in 45°C water for 6 s. Moreover, this flexible ZIB displayed nearly unchanged charge/discharge curves after repeated bending–recovery processes, indicating its potential application in multifunctional and highly durable energy storage device.

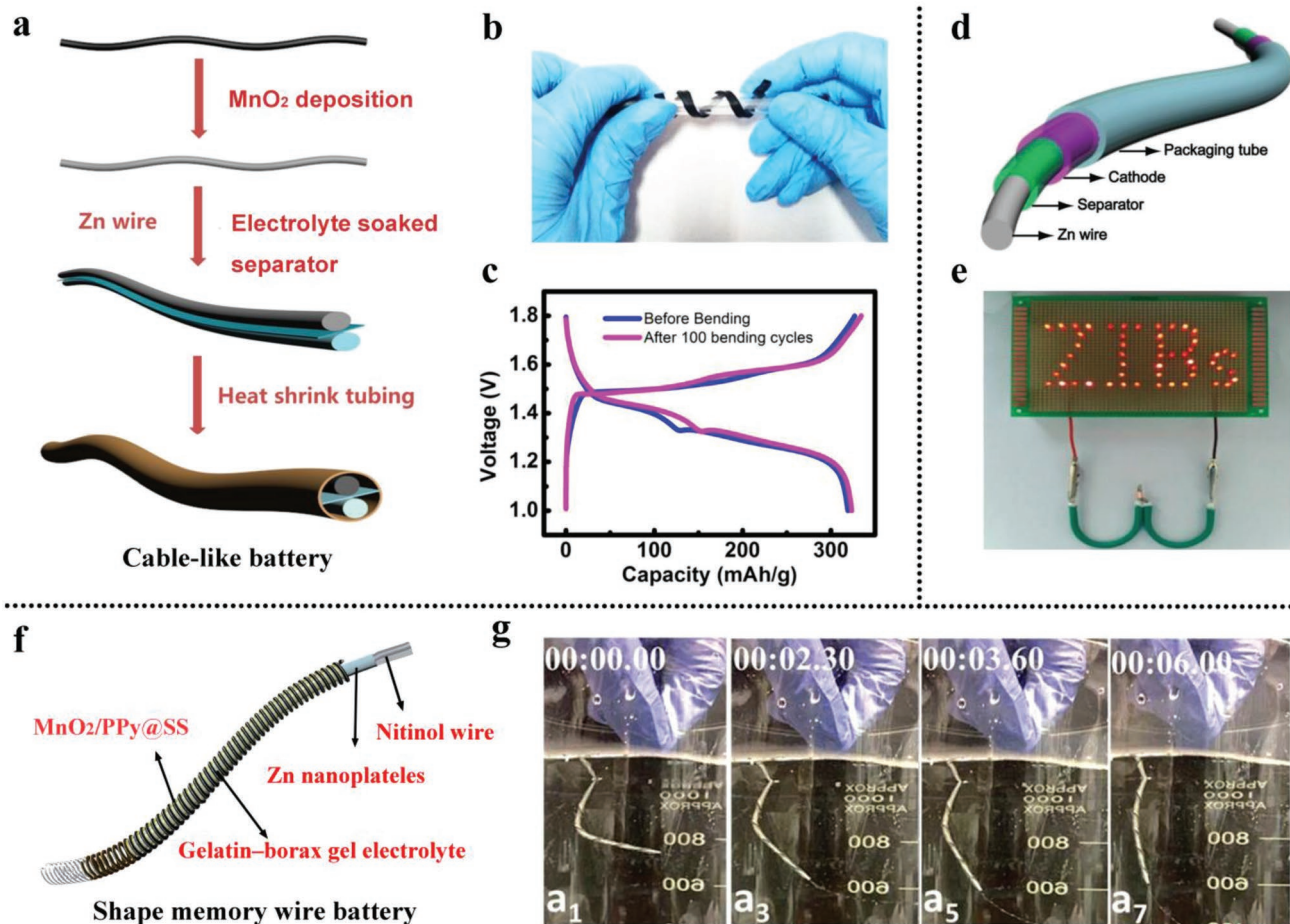


Figure 5. a) Schematic illustration for the preparation process of a Zn–MnO₂ cable battery based on MnO₂@CNT fiber cathode and Zn wire anode. b) The photograph of the Zn–MnO₂ cable battery, which can be twisted around a roller pen. c) Charge–discharge curves of a Zn–MnO₂ cable battery before and after 100 bending cycles. a–c) Reproduced with permission.^[60] Copyright 2018, American Chemical Society. d) Schematic diagrams of cable-type quasi-solid-state zinc–organic batteries. e) Photograph of the cable-type zinc–organic batteries powering an LED array. d,e) Reproduced with permission.^[61] Copyright 2018, Wiley-VCH. f) Schematic diagram of the structure of a shape–memory wire battery. g) Fast shape-recovery process of a deformed wire battery within 6 s in 45 °C water. f,g) Reproduced with permission.^[62] Copyright 2014, the Royal Society of Chemistry.

3.2. Flexible 1D Zinc-Ion Batteries with Carbon-Based Anodes

Although the metal electrodes have high electrical conductivity and mechanical strength, the use of metallic wire inevitably reduces the flexibility and energy density of the 1D battery. Toward this end, Li et al. designed an elastic yarn ZIB only with double-helix carbon nanotube yarns substrate.^[63] The fabrication process of this yarn ZIB was shown in Figure 6a. For the first, the MnO₂ cathode and Zn anode was uniformly loaded on double-helix CNT fibers surface, respectively. After that, the two fiber electrodes were wrapped on an elastic fiber in a parallel manner. Subsequently, GPE was uniformly coated on the surface of yard electrode. In the end, a fiber-shaped ZIB with high elasticity was obtained after being encapsulated in eco-flex silicone. Notably, to obtain highly flexible and stretchable yarn ZIB, the authors introduced a polyacrylamide (PAM)-based electrolyte. This electrolyte possessed an interconnected network of polyacrylamide chains connected by hydrogen bonds and covalent cross-links (Figure 6b), demonstrating a

high stretchability to 3000% strain and good tensile strength (Figure 6c). Moreover, the PAM-based electrolyte also exhibited high ionic conductivity. Benefitting from these advantages of the electrolyte, this ZIB showed high specific capacity and volumetric energy density as well as stable cycling performance. More encouragingly, this elastic yarn ZIB demonstrated excellent flexibility (Figure 6d), stretchability (Figure 6e) and superior waterproof capability (Figure 6f). In practical applications, the yarn ZIBs could be woven into a battery textile to power the LED belt and the electroluminescent panel (Figure 6g–j). Thanks to the above features, the as-fabricated elastic yarn ZIB held a great promising for powering the sensors, robotics, and implantable medical devices as a flexible energy storage device.

4. Flexible 1D Zn–Air Batteries

Compared to metal ion batteries with closed systems, metal–air batteries have received numerous attentions in recent years

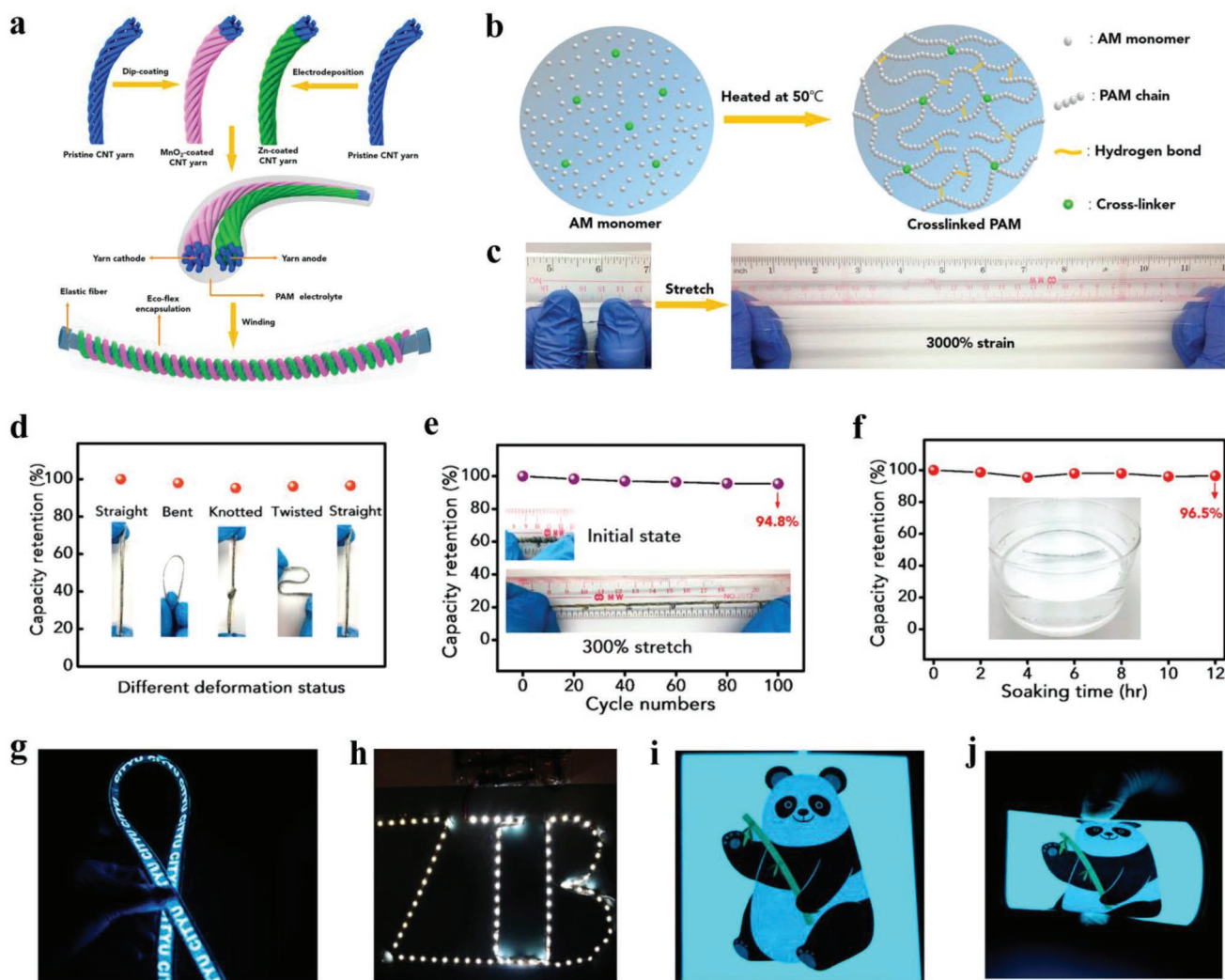


Figure 6. a) Schematic diagram of the fabrication process of the yarn ZIB. b) Schematic diagram of the fabrication of the cross-linked PAM-based electrolyte. c) Relaxed (left) and elongated (right) state of the cross-linked PAM. d) Capacity retention of the yarn ZIB in various deformation states. e) Dependence of capacity retention on cycle number with a strain of 300%. f) Superior waterproof ability of the yarn ZIB. g–j) Photographs of the yarn ZIB powering an electroluminescent panel and an LED belt. a–j) Reproduced with permission.^[63] Copyright 2018, American Chemical Society.

due to their extremely high-energy potentiality.^[64] The metal–air batteries have a characteristic half-open system in which the cathode material, oxygen, can be accessed from the environment.^[65] Among various metal–air batteries, ZABs were identified as the most desirable and relatively mature energy storage system due to their high theoretical energy density (1086 Wh kg⁻¹), low cost, and rich resource.^[66] Notably, owing to the use of high stable Zn anode and aqueous electrolyte, ZABs are always nontoxic, environmentally friendly, and safe to handle.^[67] These unique advantages make ZABs promising for wearable electronics, in which security issues are extremely critical.^[68–70] Therefore, intensive research interest has been attracted recently to explore flexible ZAB, especially in 1D type. To construct high-performance 1D ZABs with excellent flexibility, great efforts has been made in items of flexible air cathode, electrolyte, and Zn metal anode.

4.1. Flexible Air Cathode

The air cathode, consisting of a porous current collector and active materials, is an important part of ZABs wherein the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) take place.^[71–74] Unfortunately, conventional electrodes like carbon paper usually possess a rigid substrate, becoming unavailable in flexible device. To this end, tremendous efforts have been devoted to exploring novel and flexible air electrode with high flexibility and electrochemical performances.

Spraying active materials on a flexible substrate is a simple and conventional method for the fabrication of flexible air electrode. Recently, Li et al. have made the bifunctional air electrodes by spraying the bifunctional catalyst on the flexible carbon fibers (Figure 7a).^[75] The bifunctional catalyst composed of N-doped rGO and ultrathin mesoporous Co₃O₄ nanosheets, exhibited a uniform layer-by-layer morphology.

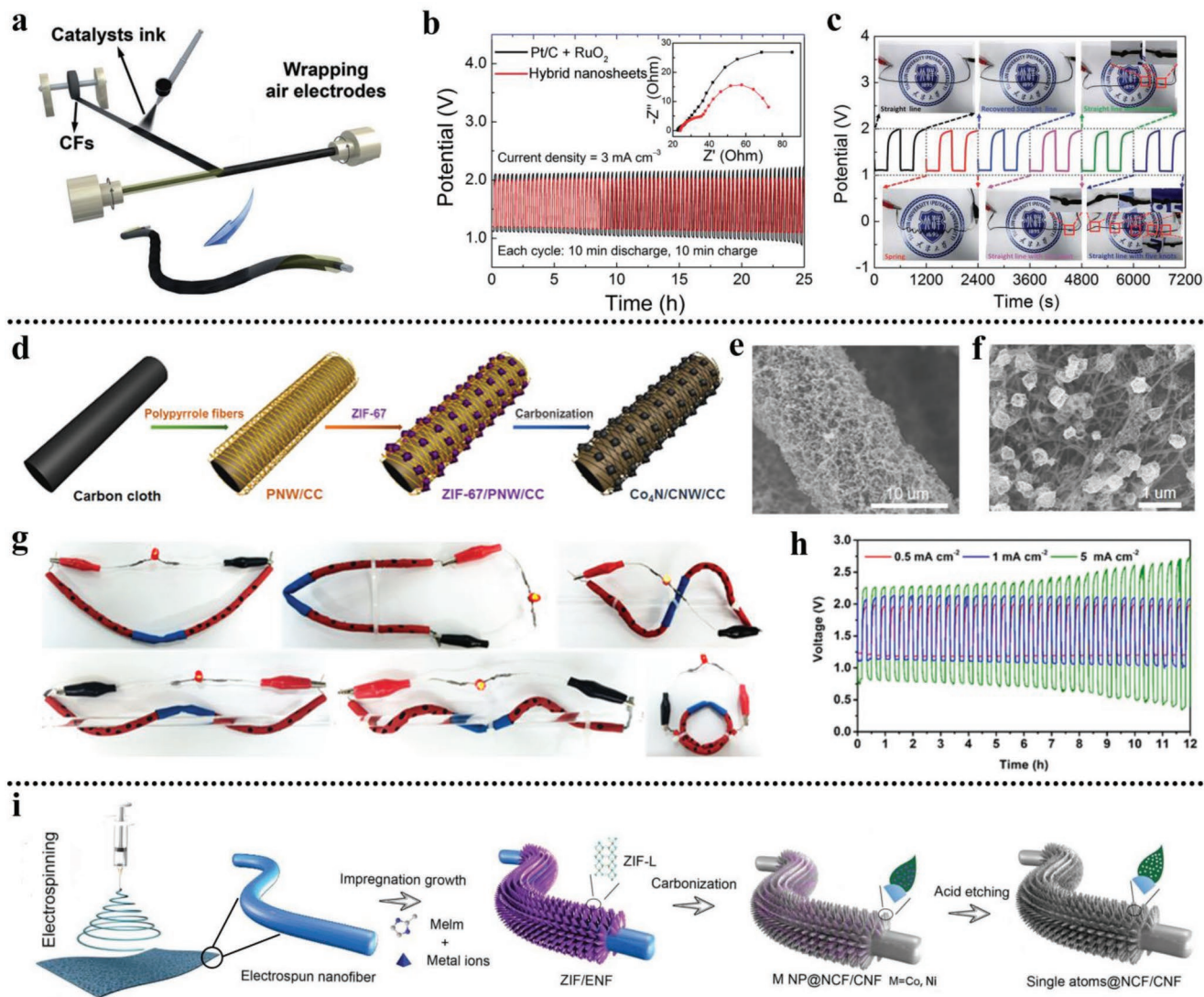


Figure 7. a) Schematic illustration of the fabrication process of an air electrode and the fiber-shaped ZAB. b) Galvanostatic discharge and charge curves of the fiber-shaped ZAB with different catalysts. c) Galvanostatic discharge and charge curves of the fiber-shaped ZAB under different conditions. a–c) Reproduced with permission.^[75] Copyright 2018, Wiley-VCH. d) Scheme of the synthesis of a $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$ electrode. e, f) Low- and high-magnification SEM images of the $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$ electrode. g) Photograph of the cable-type ZAB under various bending and twisting conditions. h) Galvanostatic discharge/charge cycling curves at different current density. d–h) Reproduced with permission.^[78] Copyright 2016, American Chemical Society. i) Schematic illustration of the “impregnation–carbonization–acidification” process for scalable fabrication of M SA@NCF/CNF film air cathode. Reproduced with permission.^[83] Copyright 2019, Wiley-VCH.

Owing to favorable advantages including high surface area, mesoporous structure, and the significant synergy effect between N-doped rGO and ultrathin Co_3O_4 nanosheets, this bifunctional catalyst exhibited superior activity and electrochemical stability for both ORR and OER. Furthermore, based on this bifunctional air cathode, a fiber-shaped ZAB was successfully assembled via wrapping the air cathode around the GPE-coated Zn wire (Figure 7a). Thanks to the excellent catalytic activity of the bifunctional electrode, this fiber-shaped ZAB showed excellent discharge and charge polarization properties and stable cycling performance, preceding the ZAB with commercialized Pt/C+RuO₂ electrode (Figure 7b). Moreover, this fiber-shaped ZAB could sustain various severe deformations without sacrificing electrochemical performance

(Figure 7c), demonstrating potentially applied in wearable electronics.

Compared with the traditional sprayed air electrode, free-standing air cathodes via direct growth of active materials on flexible substrates are more favorable for flexible batteries, due to their robust electrode structure and perfect mass transfer network.^[76,77] Therefore, Meng et al. developed a flexible, self-standing, and bifunctional air electrode in which cubic Co_4N nanoparticles decorated carbon fibers network rooted on carbon cloth (CC) ($\text{Co}_4\text{N}/\text{CNW}/\text{CC}$, Figure 7d–f).^[78] Owing to the stable hierarchical conductive network structure and the synergy effect of Co–N–C and Co_4N , the as-prepared $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$ demonstrated superior catalytic activities and stabilities for both OER and ORR. Encouragingly, a cable-type flexible ZAB

based on the $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$ electrode was successfully fabricated, which exhibited good flexibility (Figure 7g) and excellent rechargeable performance (Figure 7h). The above favorable characteristics make this cable-type ZAB promising for wearable electronic devices. Recently, Guan et al. also synthesized a flexible and binder-free air cathode by using CC as substrate to grow Co/CoN_x nanoparticles decorated nitrogen-doped carbon nanoarray.^[79] Inspiringly, a coaxial fiber-shaped ZAB built with it demonstrated high volumetric power density and excellent flexibility.

Another crucial approach for preparation of self-standing electrodes is electrospinning technique. Electrospun nanofiber is considered as the one of the most promising flexible substrate due to its favorable properties, such as controllable chemical composition, air permeability, good conductivity, light weight and excellent flexibility.^[80–82] Recently, Ji et al. proposed a facile and scalable strategy to fabricate the binder-free flexible air electrode by using electrospun nanofibers as substrate.^[83] As illustrated in Figure 7i, the polyacrylonitrile (PAN) nanofibers were produced through an electrospinning process first. Then, leaf-like Co-ZIF-Ls grew on the electrospun nanofibers by impregnation growth process. After pyrolysis and subsequent acidification processes, a self-standing flexible air electrode was obtained. Owing to the optimized single-atom active sites and hierarchically porous architectures, this flexible air electrode exhibited excellent bifunctional electrochemical activity, superior durability, and high flexibility. Considered that electrospinning process could fabricate flexible carbon substrate in a large-scale and continuous way; it is expected to promote the development of flexible 1D ZAB for future application.

4.2. Electrolyte

The electrolyte of ZABs composed of water and metal salts, is the medium for the transport of Zn ion and oxygen during the battery operation.^[84] Although, liquid electrolytes have been frequently employed in conventional ZABs, it is not suitable for flexible ZABs which may cause leakage of the electrolyte upon repeated deformation, resulting in the failure of battery.^[85] For this purpose, solid-state electrolytes are considered favorable for flexible 1D ZAB which function as electrolytes and simultaneously prevent the internal short-circuiting of battery.^[86]

For preparation of the solid-state electrolyte, the KOH-based hydrogel polymer electrolytes have been frequently investigated with various polymers, such as poly(vinyl alcohol) (PVA), poly(epichlorohydrin-co-ethylene oxide), and poly(acrylic acid).^[87–91] Generally, the fabrication process of this hydrogel polymer electrolyte is dissolved KOH and PVA into deionized water to form a homogeneous solution at $\approx 90^\circ\text{C}$ under stirring, following by freezing the gel into the solid state.^[92] Recently, Xu et al. developed a new GPE with improved the mechanical properties by adding poly(ethylene oxide) (PEO) into the PVA-based GPE (Figure 8a).^[93] The obtained freestanding GPE was flexible and stretchable (Figure 8b), and could deliver a high ionic conductivity of 0.3 S cm^{-1} (Figure 8c). Soon afterward, Park et al. demonstrated a novel GPE based on gelatin (GGPE).^[94] This GPE with high conductivity, low concentrations of KOH

(0.56 wt%), and high flexibility, ensured leak-free solid-type behavior. For further application, this GGPE was employed in cable-type flexible ZAB as illustrated in Figure 8d–f. Additionally, thanks to the high conductivity and flexibility of the GGPE, the cable-type flexible ZAB demonstrated a stable discharge curve even under bending conditions (Figure 8g).

4.3. Zinc Metal Anode

The inherent safety of Zn means that metallic Zn can directly use in ZAB as metal anode. However, the commercial Zn wires cannot satisfy the requirement of excellent flexibility when directly applied in the 1D flexible ZAB. Thus, some modifications of the Zn anode such as optimization of structures and materials are urgently needed to improving the flexibility and performances for 1D flexible ZAB. To this end, Xu et al. had proposed a spring structure Zn electrode with high flexibility and stretchability to be used in a fiber-shaped ZAB.^[93] As shown in Figure 9a, the Zn wire was first coiled onto a steel rod. After removing the Zn wire from the rod, the Zn spring electrode was obtained. Based on this flexible and stretchable Zn spring electrode, the prepared fiber-shaped ZAB demonstrated high flexibility and stretchability as well as excellent mechanical stability with its discharge curves unchanged even under bending and stretching conditions (Figure 9b–e).

To meet the demands of wearable and portable devices, the future ZAB should be characterized with high flexibility and mechanical strength, small scale, and low weight. Likewise, the electrode should also possess the above characterizations more than a stable electrochemical performance. However, metallic Zn wire is rigid and heavy, which is unfavorable for applied in future wearable electronics. With that in mind, Chen et al. had prepared Zn-plated cotton yarn anode to replace Zn wire.^[95] The fabrication process of the Zn electrode was shown in Figure 9f, a cotton yarn was first coated with Cu by electroless plating. Subsequently, metallic Zn was uniformly covered on Cu surface by electrodeposition. This Zn-plated cotton yarn possessed high flexibility and mechanical stability, enabling that 1D ZABs based on it were highly flexible and could be deformed into various shapes without sacrificing its discharge capability (Figure 9g).

5. Flexible 1D Li–Air Batteries

Compared with the above 1D batteries, 1D LABs have gained increasing attentions because of their half-open system and highest theoretical energy density (3600 Wh kg^{-1}).^[96,97] Although great progresses have been made to improve the performance of LAB,^[98] many difficulties and challenges for practical application of 1D LAB still exist, especially in achieving excellent mechanical flexibility and high energy storage capability at the same time. Similar to that of 1D ZABs, the designs of 1D LABs are mainly for air cathode, electrolyte, and metal anode. Unlike the aqueous electrolytes of ZABs, the electrolytes in LABs are organic. Therefore, the requirements of 1D LABs are different from that of 1D ZABs, especially in the structure of air cathode and the protection of metal anode.^[99]

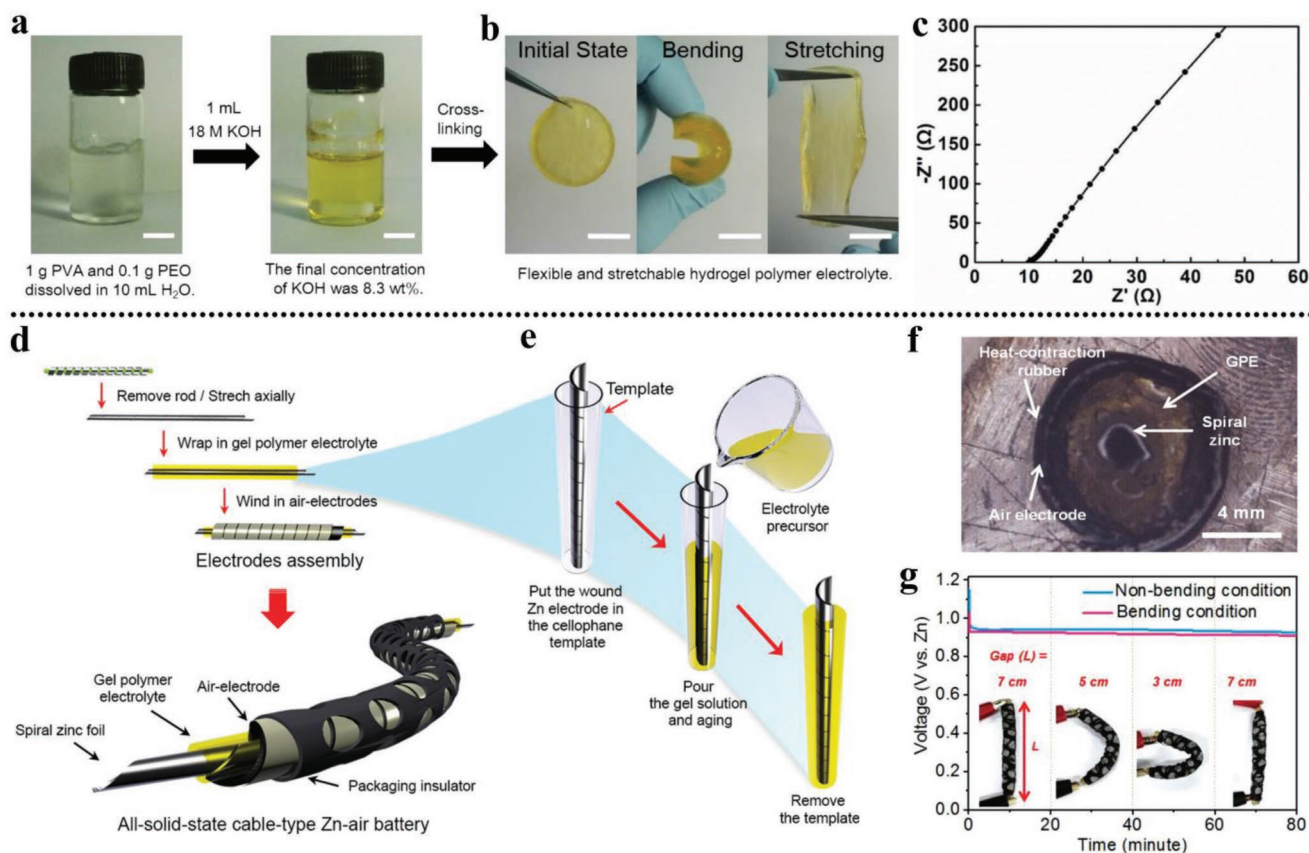


Figure 8. a) Photographs of the synthesis process of a hydrogel polymer electrolyte solution. b) Photographs of a freestanding hydrogel polymer electrolyte after crosslinking. c) AC impedance spectra of the hydrogel polymer electrolyte at a frequency range of 1000 kHz to 0.01 Hz. a–c) Reproduced with permission.^[93] Copyright 2015, Wiley-VCH. d, e) Schematic diagram of the all-solid-state cable-type flexible ZAB assembly and coating process of GGPE. f) Cross-sectional image of the cable-type flexible ZAB. g) Discharge curves of cable-type ZAB by applying bending strain every 20 min. d–g) Reproduced with permission.^[94] Copyright 2015, Wiley-VCH.

5.1. Flexible Air Cathode

Like the reactions in ZABs, LAB reactions are the ORR and OER under the action of catalysts in essence, thus meaning that air cathodes in LABs should possess highly catalytic activity. On the other hand, the discharge products generated in LABs are absolutely insoluble, which also required air cathodes with hierarchical porous structure to accommodate the products.^[100] More importantly, to meet the requirements of flexible device for bending, wrinkling, stretching, the air cathodes should be highly flexible and mechanically stable.

CC weaved with carbon fibers has been widely used as a substrate in flexible air electrode due to the excellent mechanical flexibility and high electrical conductivity. Recently, Zhang and co-workers had prepared a series of flexible air electrode by painting active materials on the surface of CC.^[101,102] Inevitably, PVDF binder was used to anchor the active materials on CC substrate in this process, while it had been proved to be unstable in the presence of superoxide radicals.^[103] Therefore, this type of electrodes always exhibited unsatisfied performance in LABs. To avoid the use of binders, it is necessary to develop freestanding air electrode by directly grown catalysts on a flexible substrate. For instance, Liu et al. fabricated a self-standing and highly flexible air electrode via in situ grown TiO₂ nanowire

arrays on CC (NAs/CT) (Figure 10a).^[104] This air cathode exhibited stable catalytic activity, high chemical and mechanical flexible stability, as well as excellent electrochemical performance. Considering the multifunctional properties of the TiO₂ NAs/CT cathode, it is expected as a favorable flexible air electrode for the fabrication of flexible 1D LABs.

Compared with CC, aligned CNT sheets are considered more suitable for flexible device due to their light weight, high flexibility and electrical conductivity.^[105] As a result, Zhang et al. fabricated a coaxial-fiber flexible LAB by using the aligned CNT sheets as air cathode.^[106] As illustrated in Figure 10b, a layer of GPE was first coated onto the Li wire, following by wrapping the aligned CNT sheets around. Finally, a coaxial-fiber flexible LAB was obtained after encapsulation in a punched heat-shrinkable tube, exhibiting a discharge capacity of 12 470 mAh g⁻¹ and long cycle life of 100 cycles in air.

Although, numerous flexible air electrodes have been constructed based on CC and spinnable CNT arrays, their inferior properties including low mechanical strength and poor structural stability are still far away from the demands of flexible 1D LABs that required repeated twisting and bending. Stainless-steel (SS) mesh with high electrical conductivities and good structural robustness has been regarded as a favorable substrate for flexible LABs. Recently, Yang et al. constructed a

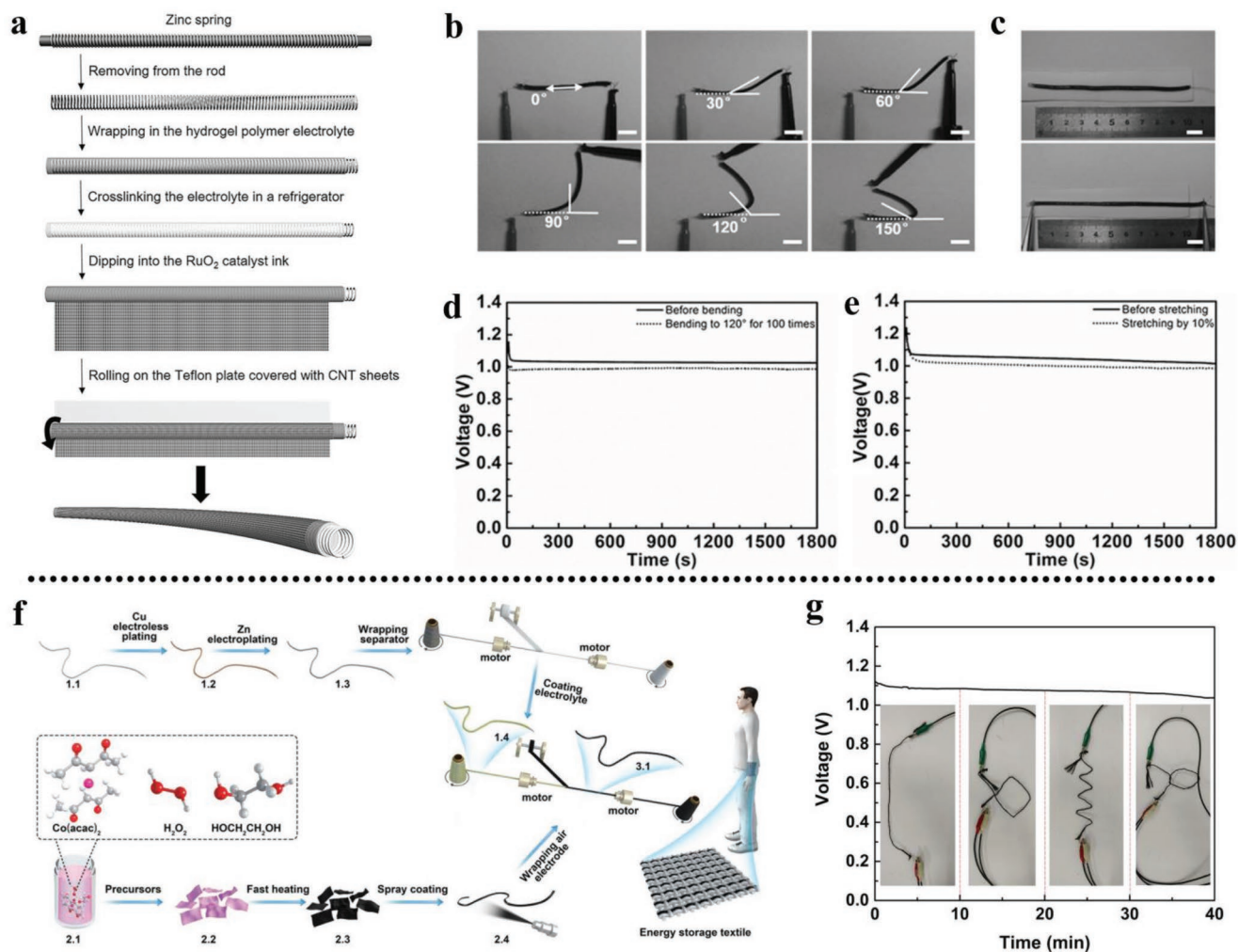


Figure 9. a) Schematic illustration to the fabrication of the fiber-shaped ZAB. b) Photographs of a fiber-shaped ZAB bent to increasing angles. c) Photographs of a fiber-shaped ZAB before and after stretching by 10%. d) Discharge curves of the fiber-shaped ZAB with a length of 5 cm at a current density of 1 A g^{-1} before and after bending to 120° for 100 cycles. e) Discharge curves of the fiber-shaped ZAB with a length of 10 cm at a current density of 1 A g^{-1} before and after stretching by 10%. a–e) Reproduced with permission.^[93] Copyright 2015, Wiley-VCH. f) Schematic diagram of the fabrication procedure of the yarn-based ZAB. g) Discharge curves of the yarn-based ZAB caused by deformation and knotting of the battery into various shapes. f,g) Reproduced with permission.^[95] Copyright 2018, Wiley-VCH.

flexible air electrode via directly growing N-doped CNTs on SS mesh (N-CNTs@SS) surface, building a robust interconnected hierarchical carbon network (Figure 10c).^[107] Nota that this air cathode showed excellent characteristics covering suitable hierarchical structure, high electrical conductivity, great structure stability and flexibility. Profiting from these advantages of the N-CNTs@SS cathode, a cable-type flexible LAB built with it delivered superior electrochemical performance, including high specific capacity, excellent rate capability and long cycle stability. Furthermore, this cable-type battery also exhibited good mechanical stability and flexibility as its capacity without change even under the various bent and twisted conditions (Figure 10d,e).

Replacing traditional lamellar substrates with filiform substrates, Lin et al. lately introduced an unprecedented air electrode with self-standing structure by using conductive metal wire and wearable cotton fiber yarn as the substrate to absorb

RuO_2 -coated N-doped CNTs ink (Figure 10f).^[108] With this novel air cathode, a wire-shaped Li–O₂ battery achieved a high discharge capacity of 1981 mAh g^{-1} . Notably, even under the bending conditions, the battery exhibited outstanding electrochemical stability with no obvious degradation in capacity after 100 cycles (Figure 10g). Moreover, an LED remained constantly lit by this wire-shaped Li–O₂ battery even under bending and knotting conditions, demonstrating it is highly flexible (Figure 10h).

In the above air electrodes, carbon materials have never been avoided, either as substrates or as active materials. However, carbon materials have been proved to be unstable in LABs, which can react with the oxidative products (e.g., LiO₂ and Li₂O₂), generating irreversible side products. Notably, these insoluble side products cover the active sites on the air electrode surface, giving rise to the passivation of the electrode or even death of the battery.^[109–111] Hence, developing flexible

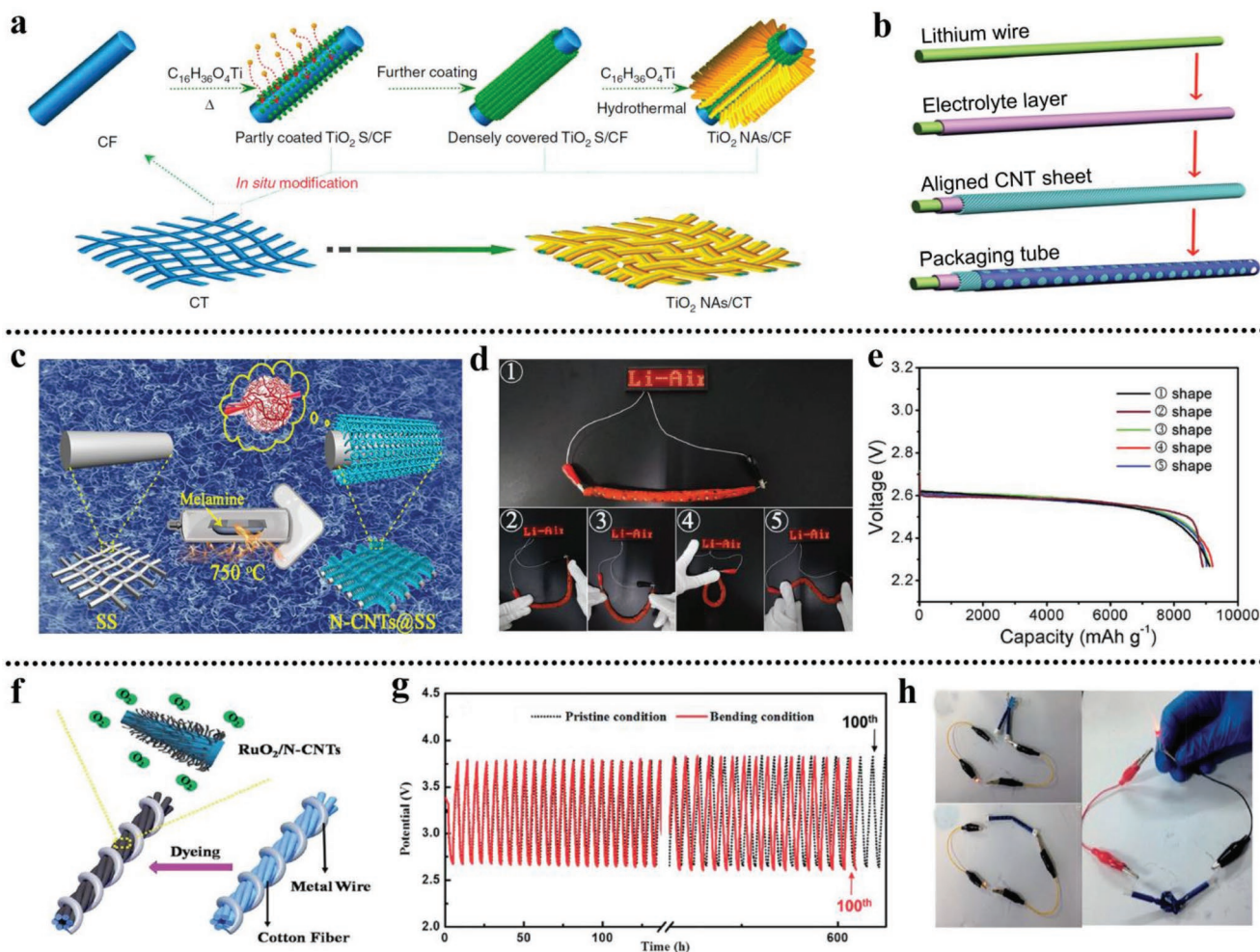


Figure 10. a) Schematic of the design and preparation of the TiO₂ NAs/CT. Reproduced with permission.^[104] Copyright 2015, Nature Publishing Group. b) Schematic of the fabrication of the fiber-shaped LAB. Reproduced with permission.^[106] Copyright 2016, Wiley-VCH. c) Schematic of the synthesis process of the N-CNTs@SS. d,e) Cable-type flexible LAB powering a commercial red LED display screen under various bending and twisting conditions (d) and the corresponding discharge curves (e). d,e) Reproduced with permission.^[107] Copyright 2018, Wiley-VCH. f) Schematic of the preparation of the metal/cotton yarns electrode. g) Charge/discharge curves of the wire-shaped LABs under pristine and bending conditions. h) A LED powered by the wire-shaped LABs. f–h) Reproduced with permission.^[108] Copyright 2017, the Royal Society of Chemistry.

air electrode with high-graphitization-degree carbon materials or no-carbon materials to prevent the corrosion of electrode is important for flexible 1D LABs.^[112]

5.2. Electrolyte

The electrolyte is the medium for the transport of Li ion and oxygen during LABs operation. As a result, an ideal electrolyte applied in LABs should possess high solubility of oxygen and lithium salt, high ionic conductivity and good chemical stability. Nowadays, a series of electrolytes have been explored as the development of flexible 1D LABs.^[113]

Compared with other liquid electrolyte systems, lithium triflate (LiCF₃SO₃) in tetraethylene glycol dimethyl ether (TEGDME) is considered as the most promising candidate for LAB due to its low volatility and high stability.^[114] Consequently, Zhang et al. fabricated a series of flexible 1D LABs by using

this kind of electrolyte, all of which showed excellent electrochemical stability.^[101,102] Beyond that, owing to good thermal stability, incombustible, and high oxidation potential, ionic liquids have been applied in LABs as a new type electrolyte.^[115,116] Recently, Yang et al. had developed an ionic liquid-based electrolyte (0.5 M LiTFSI dissolved in 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide) for application in the cable-type flexible LAB. Benefiting from uniquely advantageous of the liquid electrolyte, the as-fabricated flexible battery could deliver a capacity of 1000 mAh g⁻¹ even after 121 cycles at a current density of 500 mA g⁻¹, demonstrating its excellent cycle stability.^[107]

However, the liquid electrolyte is extremely volatile and easy to leak, leading to serious safety concern for practical applications, especially in the half-open system of LAB. To avoid the use of liquid electrolyte, Zhang et al. proposed a GPE for the coaxial-fiber flexible LAB (Figure 11a).^[106] This GPE possessed high ionic conductivity of 1.15 mS cm⁻¹ (Figure 11b) and a

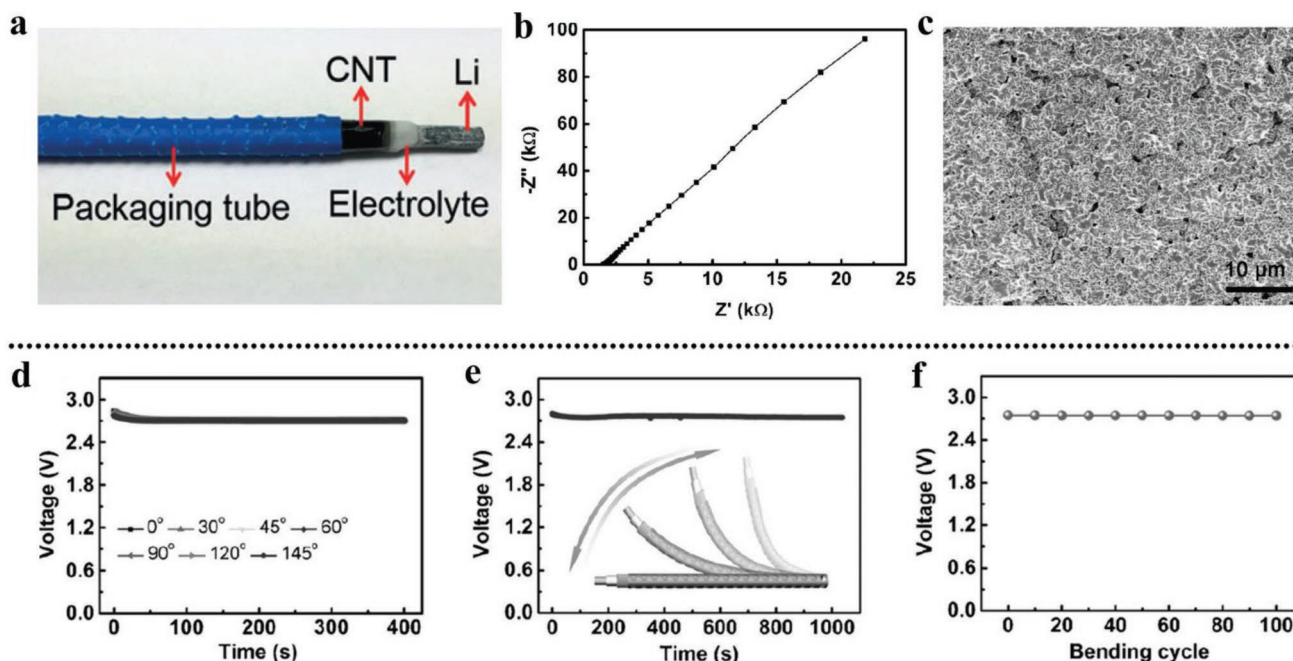


Figure 11. a) Photograph of the fiber-shaped LAB with GPE. b) EIS of the GPE in a frequency range of 1 Hz to 100 kHz. c) SEM image of GPE. d,e) Discharge curves under different bending angles. f) Discharge voltage on different bending cycle at a bending angle of 90°. a–f) Reproduced with permission.^[106] Copyright 2016, Wiley-VCH.

porous structure (Figure 11c), benefiting for ion diffusion. Note that the coaxial-fiber flexible LAB with the GPE exhibited high flexibility, it could operate stably even under bending process (Figure 11d,e). In addition, the voltage profiles could be maintained even after bending for 100 cycles (Figure 11f). These results demonstrated that the GPE possess excellent mechanical stability and can endure various deformation modes.

5.3. Li Metal Anode

Due to the flexibility and plasticity of Li metallic wires, they are usually directly used in flexible 1D LABs as metal anode. However, the moisture and water in the atmosphere environment or emergency situation would react violently with unprotected Li metal, causing the death of the battery or even serious safety accident. Therefore, the protection of Li metal in the half-open system is the premise and guarantee for the practical application of 1D LAB.

Recently, Liu et al. had proposed and demonstrated a cable-type water-survivable flexible LAB, protected by a freestanding GPE.^[101] The fabricate strategy of the LAB was shown in Figure 12a. To protect the Li metal anode, the Li metal rod was first coated with the precursor of the GPE, following by being exposed to UV irradiation for 20 s to form a white, solidified, nonsticky GPE on the Li metal rod. It should be noted that the GPE was hydrophobic with a water droplets contact angle (CA) on its membrane of 98.8° (Figure 12b), meaning that it could protect the Li anode from corrosion of water and moisture. To illustrate this, the GPE-coated Li rods were immersed in

water. As shown in Figure 12c, the protected Li rod was stable in water. In marked contrast, the unprotected Li rods reacted immediately and violently with water, accompanied by a large amount of bubbles. Due to the superior hydrophobicity of the GPE, the cable-type flexible Li–O₂ battery protected with it was waterproof, which could operate properly even under water (Figure 12d). Additionally, Yin et al. also design a hybrid separator (PIPV) composed of polyimide (PI) and PVDF–HFP to protect the Li metal anode.^[102] As shown in Figure 12e, the Li piece was first packed with PI membrane, following by injection of PVDF–HFP solution between them. After drying in argon atmosphere, the PIPV protected Li metal anode was obtained. Encouragingly, this PIPV membrane was also hydrophobic and waterproof. A highly safe cable-type Li–O₂ battery fabricated with it exhibited superior flexibility and water resistance, which could normally work under water even in a bending condition (Figure 12f).

Apart from the protection of Li anode by modifying the surface of Li metal, selective isolation of moisture and water from the external environment is also an effective way for protecting Li metal. Considered that low-density polyethylene (LDPE) film with nonpolar molecular structure possesses a high selectivity for nonpolar O₂ molecules and can prevent polar moisture molecules across from the film, Wang et al. had fabricated a fiber-shaped LAB with LDPE film to prevent water erosion.^[117] Figure 12g shows the fabrication process of the flexible fiber-shaped LAB. First, Li wire was coated with GPE, following by being wound with aligned CTN sheets as the cathode. Subsequently, LDPE film was wrapped around the battery core. After being packed in a porous heat shrink tube, a fiber-shaped LAB was constructed. Notably, with the aid of the selective LDPE

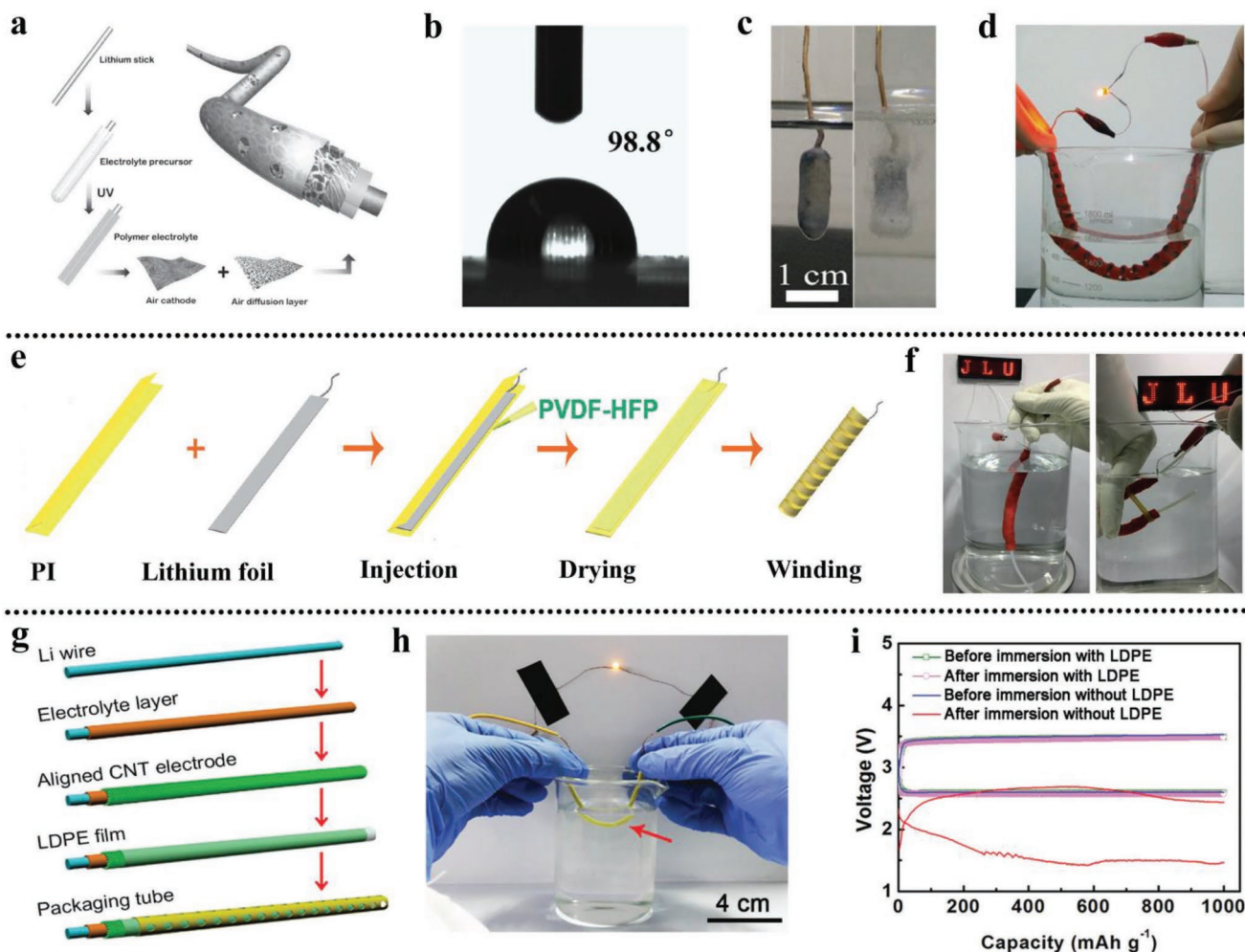


Figure 12. a) Schematic of the design and preparation of the cable-type and water-survivable flexible LAB. b) Water contact angle of GPE. c) The photographs of an Li rod immersed in water with (left) and without (right) the protection of the GPE membrane. d) Cable-type flexible LAB powering a red LED in water. a–d) Reproduced with permission.^[101] Copyright 2016, Wiley-VCH. e) Schematic for the preparation of PIPV separator protected Li foil. f) Highly safe flexible Li–O₂ batteries powering a commercial red LED display screen in water. e, f) Reproduced with permission.^[102] Copyright 2018, Wiley-VCH. g) Schematic illustration to the fabrication of the flexible fiber-shaped LAB with LDPE film. h) A flexible fiber-shaped LAB powering an LED in water. i) Discharge/charge curves of the flexible fiber-shaped LAB before and after immersion in water with and without LDPE film. g–i) Reproduced with permission.^[117] Copyright 2018, Wiley-VCH.

film, this battery was water survivable, which could power a yellow LED stably even when it was immersed in water (Figure 12h). Additionally, under the protection of LDPE film, this flexible fiber-shaped LAB worked normally with its electrochemical behavior remaining unchanged even after immersion in water (Figure 12i). More encouragingly, the LDPE film can also suppress side reactions, preventing the conversion of Li₂O₂ to LiOH and Li₂CO₃. As a result, the flexible fiber-shaped LAB exhibited a long cycle life up to 610 cycles in ambient atmosphere.

Besides LABs, other flexible 1D batteries with high theoretical energy density, including Na–air battery, Li–CO₂ battery and Li–S battery also have been explored in recent years.^[118–121] Although, the application of these batteries is limited by many factors, such as working environment and safety issues, they are also expected to power the flexible electronic devices in specific situations.

6. Flexible Fabric Batteries

Textiles are the flexible materials consisting of a network of natural or artificial fibers, forming by a variety of techniques such as weaving, knitting, tatting and etc. As a result, most of the textiles are highly flexible and can easily restore its original state after being bent or wrinkled. Inspired by traditional textiles with flexible interconnected network structure, the 1D battery could be woven into fabric batteries to bear the huge deformations from stretching, bending and folding (Figure 13a).^[43] Additionally, fabric batteries composed of fiber batteries exhibit increased energy storage capability, enabling the future wearable electronics with long working time.

Nowadays, the basic methods applied in fabric batteries are to integrate 1D battery into a flexible textile matrix. For instance, Peng's group fabricated flexible coaxial fiber LIB and subsequently woven it into a flexible textile (Figure 13b).^[31]

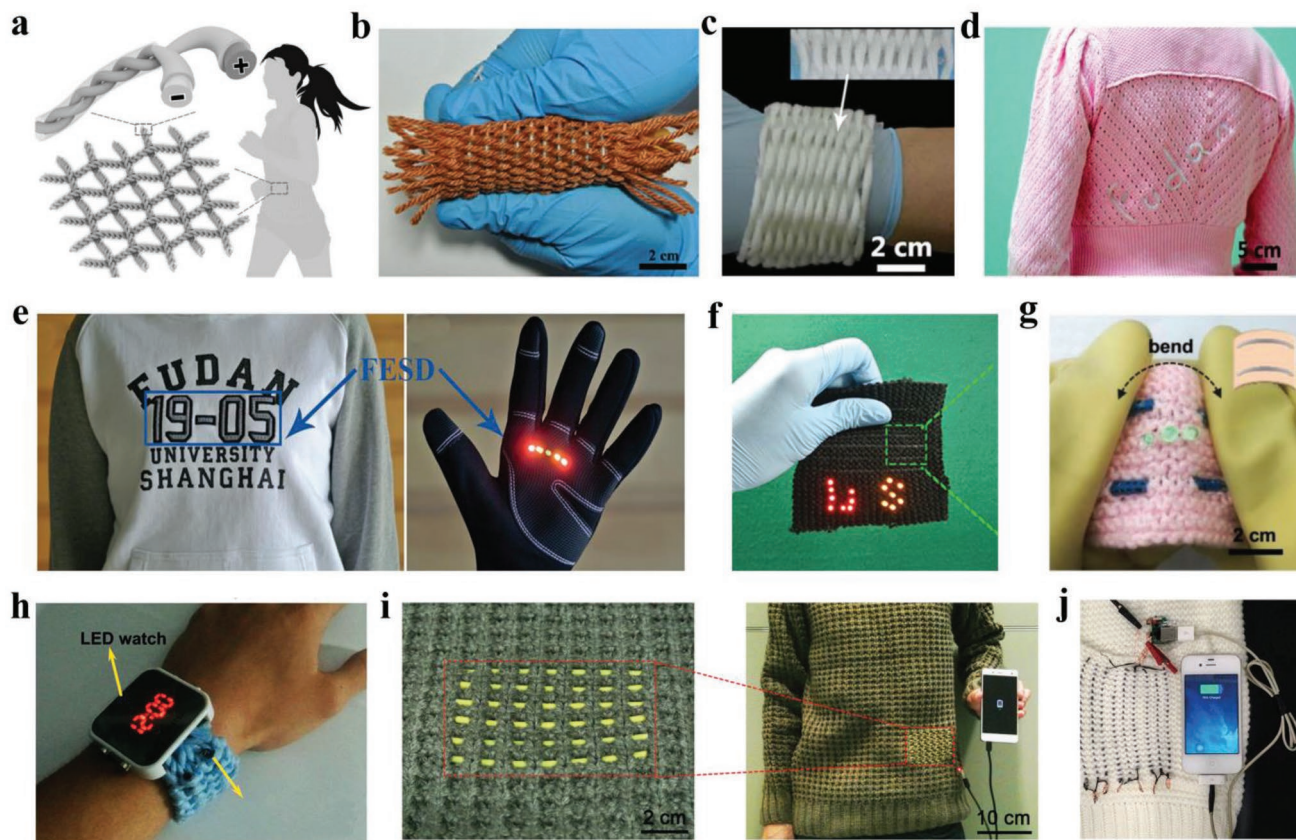


Figure 13. a) Schematic diagram of 1D batteries potentially applied in wearable applications. b–d) 1D batteries woven into various flexible textiles. e–h) LED light and watch powered by wearable textile batteries. i, j) Mobile phone charged by wearable textile batteries. a) Reproduced with permission.^[43] Copyright 2017, Wiley-VCH. b) Reproduced with permission.^[31] Copyright 2014, American Chemical Society. c, d) Reproduced with permission.^[45] Copyright 2014, the Royal Society of Chemistry. e) Reproduced with permission.^[44] Copyright 2015, Wiley-VCH. f) Reproduced with permission.^[121] Copyright 2016, Wiley-VCH. g) Reproduced with permission.^[120] Copyright 2019, Wiley-VCH. h) Reproduced with permission.^[122] Copyright 2016, Wiley-VCH. i) Reproduced with permission.^[117] Copyright 2018, Wiley-VCH. j) Reproduced with permission.^[75] Copyright 2018, Wiley-VCH.

As a result, the obtained textile battery achieved a high area energy density of 4.5 mWh cm^{-2} . However, it is not enough to form battery textile alone, flexible device could well fit the dynamic motions of human body is the key to particle application. Soon afterward, their group designed a superstretchy fiber-shaped LIB, which could be woven into a bracelet textile (Figure 13c) and a knitted sweater (Figure 13d) with ease, better accommodating the movement of the human body.^[45] To further promote the practical application of fabric batteries, they implanted a hybrid energy storage fibers device into sweater and glove, successfully lightening five LED (Figure 13e).^[44] Besides, fabric batteries based on 1D Li–S batteries (Figure 13f) and Li–CO₂ batteries (Figure 13g) also exhibited excellent flexibility and potential application in wearable device as they were incorporated into flexible textile to power LEDs.^[121,120] Recently, Xu et al. designed high performance all-solid-state fiber-shaped aluminum-air batteries,^[122] which were woven into a flexible textile to power an electronic watch worn around a human wrist (Figure 13h). More encouragingly, flexible 1D Li–air and Zn–air batteries had also been successfully integrated into wearable clothes,^[75,117] which could effectively charge the smartphones, as shown in Figure 13i, j, demonstrating the real application of these fabric batteries.

7. Conclusion

Great progress has been achieved in 1D battery and a variety of models for different battery systems have been successfully demonstrated (Table 1). However, as the 1D batteries are still in their infancy, the current 1D batteries are always faced with various issues including inferior performance, high cost, less flexibility, and poor safety, far away from the practical applications demands for wearable electronics. Nowadays, the main bottlenecks impeding the commercialization of 1D battery are the following three:

- 1) The current 1D batteries deliver unsatisfied performance, such as low energy density, power density, and inferior cycle life. These are probably caused by three points. First, most of the flexible substrates currently have a low specific surface with low mass loading of active materials. As a result, the flexible 1D battery always exhibits inferior energy storage capability. To this end, development of high specific surface electrodes is critical. Second, unstable interfaces constructed by binder between the active materials and flexible substrates impede mass transfer, leading to an unsatisfied power density. What's worse, the active materials will peel

Table 1. Summary of the performances of recently reported flexible 1D batteries.

Battery	Structure	Cathode	Anode	Electrolyte	Voltage	Capacity	Ref.
LIB	Coaxial	LCO	Ni–Sn	Liquid	3.5 V	1.0 mAh cm ⁻¹	[30]
LIB	Coaxial	LMO	Si	Gel	3.4 V	106.5 mAh g ⁻¹	[31]
LIB	Coaxial	LCO	LTO	Liquid	≈2.6 V	130 mAh g ⁻¹	[32]
LIB	Twisted	MnO ₂	Li	Liquid	1.5 V	218.32 mAh g ⁻¹	[33]
LIB	Twisted	Si	Li	Liquid	0.4 V	1670 mAh g ⁻¹	[34]
LIB	Twisted	LMO	LTO	Liquid	2.5 V	138 mAh g ⁻¹	[37]
LIB	Twisted	LMO	Titania	Liquid	–	–	[38]
LIB	Twisted	LFP	LTO	Gel	≈1.9 V	110 mAh g ⁻¹	[43]
LIB	Twisted	LMO	LTO	Gel	2.3 V	120.5 mAh g ⁻¹	[44]
LIB	Stretchable	LMO	LTO	Gel	2.2 V	91.3 mAh g ⁻¹	[45]
LIB	Stretchable	LMO	LTO	Gel	2.5 V	92.4 mAh g ⁻¹	[46]
ZIB	Coaxial	MnO ₂	Zn	Gel	≈1.3 V	174.2 mAh g ⁻¹	[62]
ZIB	Twisted	MnO ₂	Zn	Liquid/Gel	1.36/1.24 V	322/290 mAh g ⁻¹	[60]
ZIB	Stretchable	MnO ₂	Zn	Gel	≈1.3 V	302.1 mAh g ⁻¹	[63]
ZAB	Coaxial	Co ₃ O ₄ /N-rGO	Zn	Gel	1.2 V	550 mAh g ⁻¹	[75]
ZAB	Coaxial	Co ₄ N/CNW/CC	Zn	Gel	1.23 V	7.5 mAh cm ⁻²	[78]
ZAB	Stretchable	RuO ₂	Zn	Gel	1.0 V	6 mAh cm ⁻³	[93]
ZAB	Coaxial	Fe/N/C-900	Zn	Gel	0.92 V	0.9 mAh cm ⁻²	[94]
ZAB	Coaxial	Co ₃ O ₄	Zn	Gel	1.0 V	7.7 mAh cm ⁻³	[95]
LAB	Coaxial	CNT	Li	Gel	2.45 V	13 055 mAh g ⁻¹	[106]
LAB	Coaxial	N-CNTs@SS	Li	Gel	≈2.6 V	≈9000 mAh g ⁻¹	[107]
LAB	Coaxial	RuO ₂ /N-CNTs	Li	Liquid	2.5 V	1981 mAh g ⁻¹	[108]
LAB	Coaxial	Super P	Li	Gel	≈2.7 V	≈4800 mAh g ⁻¹	[101]
LAB	Coaxial	Ru/CNT	Li	Liquid	≈2.7 V	4259 mAh g ⁻¹	[102]
LAB	Coaxial	CNT	Li	Gel	≈2.5 V	1000 mAh g ⁻¹	[117]

off from the flexible substrate during cycling or deformation, resulting in a bad cycle performance or even the death of battery. Fortunately, self-standing electrodes with robust interfaces are considered to solve these issues. Third, the GPEs, supposed to substitute liquid electrolyte possess lower ionic conductivity and higher interfacial resistance compared with that of liquid electrolyte, limiting the rate capability of the 1D battery. Therefore, abundant researches focused on high performance GPE are highly required.

- 2) The cost of 1D batteries should also be considered. Generally, 1D battery is mainly consisted of flexible electrodes, GPE, separator, and encapsulating materials, wherein the flexible electrode and GPE determine the cost of the battery. At present, flexible electrodes are prepared primarily by loading active materials on expensive flexible substrates with a cumbersome and energy-intensive method, which undoubtedly increased the battery cost, impeding the commercialization of the 1D batteries. Moreover, the using of GPEs greatly improve the battery safety, while the synthesization of GPEs always require complex producing processes and expensive raw materials, leading to a high cost for large-scale fabrication.
- 3) Almost all of the 1D batteries are manufactured in lab and are not yet commercialized. To achieve large-scale and low-cost fabrication of 1D batteries, preparation of flexible electrodes

with a simple, rapid and controllable process must be realized first. Lately, as manufacturing techniques rapidly developing, new manufacturing methods like 3D printing techniques are quickly emerging. These new techniques are considered feasible for production of flexible electrode with high performance and yields. Another crucial issue is to develop continuous production line for automated assembly of 1D battery. Moreover, to meet the requirements of the flexible/wearable electronics, the 1D battery must be woven into flexible, breathable and wearable textiles. To this end, continuous and efficient machine-based weaving techniques must be developed to supersede hand knitting in the laboratory.

Acknowledgements

Y.-H.Z., X.-Y.Y., and T.L. contributed equally to this work. This work was financially supported by the Ministry of Science and Technology of the People's Republic of China (Grant Nos. 2016YFB0100103 and 2017YFA0206704), the National Program on Key Basic Research Project of China (Grant No. 2014CB932300), the Technology and Industry for National Defence of the People's Republic of China (Grant No. JCKY2016130B010), the National Natural Science Foundation of China (Grant Nos. 51522101, 51471075, 51631004, and 51401084), and the China Postdoctoral Science Foundation (Grant No. 2016M601395).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

flexible 1D batteries, metal–air batteries, metal-ion batteries, wearable electronics

Received: March 28, 2019

Revised: April 13, 2019

Published online: July 22, 2019

- [1] S. Hong, S. Myung, *Nat. Nanotechnol.* **2007**, *2*, 207.
- [2] L. Wang, D. Chen, K. Jiang, G. Shen, *Chem. Soc. Rev.* **2017**, *46*, 6764.
- [3] S. Ju, A. Facchetti, Y. Xuan, J. Liu, F. Ishikawa, P. D. Ye, C. W. Zhou, T. J. Marks, D. B. Janes, *Nat. Nanotechnol.* **2007**, *2*, 378.
- [4] H. M. Lee, S. Y. Choi, A. Jung, S. H. Ko, *Angew. Chem.* **2013**, *125*, 7872.
- [5] S. Park, M. Vosguerichian, Z. Bao, *Nanoscale* **2013**, *5*, 1727.
- [6] W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang, X.-M. Tao, *Adv. Mater.* **2014**, *26*, 5310.
- [7] W. Gao, S. Emaminejad, H. Y. Nyein, S. Challa, K. Chen, A. Peck, H. M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D. H. Lien, G. A. Brooks, R. W. Davis, A. Javey, *Nature* **2016**, *529*, 509.
- [8] D. Kim, D. Kim, H. Lee, Y. R. Jeong, S. J. Lee, G. Yang, H. Kim, G. Lee, S. Jeon, G. Zi, J. Kim, J. S. Ha, *Adv. Mater.* **2016**, *28*, 748.
- [9] X. Wang, Z. Liu, T. Zhang, *Small* **2017**, *13*, 1602790.
- [10] L. Li, Z. Wu, S. Yuan, X.-B. Zhang, *Energy Environ. Sci.* **2014**, *7*, 2101.
- [11] Y. Fu, X. Cai, H. Wu, Z. Lv, S. Hou, M. Peng, X. Yu, D. Zou, *Adv. Mater.* **2012**, *24*, 5713.
- [12] K. Xie, B. Wei, *Adv. Mater.* **2014**, *26*, 3592.
- [13] H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737.
- [14] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, Z. Wang, *Adv. Mater.* **2015**, *27*, 2472.
- [15] W. Liu, M. S. Song, B. Kong, Y. Cui, *Adv. Mater.* **2017**, *29*, 1603436.
- [16] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, G. Shen, *Adv. Mater.* **2014**, *26*, 4763.
- [17] L. Hu, H. Wu, F. La Mantia, Y. Yang, Y. Cui, *ACS Nano* **2010**, *4*, 5843.
- [18] Z. Chen, J. W. F. To, C. Wang, Z. Lu, N. Liu, A. Chortos, L. Pan, F. Wei, Y. Cui, Z. Bao, *Adv. Eng. Mater.* **2014**, *4*, 400207.
- [19] B. Liu, J. Zhang, X. Wang, G. Chen, D. Chen, C. Zhou, G. Shen, *Nano Lett.* **2012**, *12*, 3005.
- [20] S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, H. Cheng, B. Lu, C. Yu, C. Chuang, T.-I. Kim, T. Song, K. Shigeta, S. Kang, C. Dagdeviren, I. Petrov, P. V. Braun, Y. Huang, U. Paik, J. A. Rogers, *Nat. Commun.* **2013**, *4*, 1543.
- [21] H. Sun, Y. Zhang, J. Zhang, X. Sun, H. Peng, *Nat. Rev. Mater.* **2017**, *2*, 17023.
- [22] L. Lu, Y. Hu, K. Dai, *Mater. Today Chem.* **2017**, *5*, 24.
- [23] X. Wang, K. Jiang, G. Shen, *Mater. Today* **2015**, *18*, 265.
- [24] Y. Zhang, Y. Zhao, J. Ren, W. Weng, H. Peng, *Adv. Mater.* **2016**, *28*, 4524.
- [25] 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.
- [26] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252.
- [27] B. Scrosati, J. Hassoun, Y. K. Sun, *Energy Environ. Sci.* **2011**, *4*, 3287.
- [28] H. Li, Z. Wang, L. Chen, X. Huang, *Adv. Mater.* **2009**, *21*, 4593.
- [29] A. Sumboja, J. Liu, W. G. Zheng, Y. Zong, H. Zhang, Z. Liu, *Chem. Soc. Rev.* **2018**, *47*, 5919.
- [30] Y. H. Kwon, S.-W. Woo, H.-R. Jung, H. K. Yu, K. Kim, B. H. Oh, S. Ahn, S.-Y. Lee, S.-W. Song, J. Cho, H.-C. Shin, J. Y. Kim, *Adv. Mater.* **2012**, *24*, 5192.
- [31] W. Weng, Q. Sun, Y. Zhang, H. Lin, J. Ren, X. Lu, M. Wang, H. Peng, *Nano Lett.* **2014**, *14*, 3432.
- [32] Z. P. Wu, K. X. Liu, C. Lv, S. W. Zhong, Q. H. Wang, T. Liu, X. B. Liu, Y. H. Yin, Y. Y. Hu, D. Wei, Z. F. Liu, *Small* **2018**, *14*, 1800414.
- [33] J. Ren, L. Li, C. Chen, X. Chen, Z. Cai, L. Qiu, Y. Wang, X. Zhu, H. Peng, *Adv. Mater.* **2013**, *25*, 1155.
- [34] H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang, H. Peng, *Adv. Mater.* **2014**, *26*, 1217.
- [35] K. S. Park, A. Benayad, D. J. Kang, S. G. Doo, *J. Am. Chem. Soc.* **2008**, *130*, 14930.
- [36] L. Zhao, Y. S. Hu, H. Li, Z. X. Wang, L. Q. Chen, *Adv. Mater.* **2011**, *23*, 1385.
- [37] 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.
- [38] T. Hoshida, Y. Zheng, J. Hou, Z. Wang, Q. Li, Z. Zhao, R. Ma, T. Sasaki, F. Geng, *Nano Lett.* **2017**, *17*, 3543.
- [39] T. A. Campbell, O. S. Ivanova, *Nano Today* **2013**, *8*, 119.
- [40] J. C. Ruiz-Morales, A. Tarancon, J. Canales-Vazquez, J. MendezRamos, L. Hernandez-Afonso, P. Acosta-Mora, J. R. Marin Rueda, R. Fernandez-Gonzalez, *Energy Environ. Sci.* **2017**, *10*, 846.
- [41] K. Fu, Y. Wang, C. Yan, Y. Yao, Y. Chen, J. Dai, S. Lacey, Y. Wang, J. Wan, T. Li, Z. Wang, Y. Xu, L. Hu, *Adv. Mater.* **2016**, *28*, 2587.
- [42] K. Sun, T. S. Wei, B. Y. Ahn, J. Y. Seo, S. J. Dillon, J. A. Lewis, *Adv. Mater.* **2013**, *25*, 4539.
- [43] Y. B. Wang, C. J. Chen, H. Xie, T. T. Gao, Y. G. Yao, G. Pastel, X. G. Han, Y. J. Li, J. P. Zhao, K. Fu, L. B. Hu, *Adv. Funct. Mater.* **2017**, *27*, 1703140.
- [44] Y. Zhang, Y. Zhao, X. Cheng, W. Weng, J. Ren, X. Fang, Y. Jiang, P. Chen, Z. Zhang, Y. Wang, H. S. Peng, *Angew. Chem., Int. Ed.* **2015**, *54*, 11177.
- [45] Y. Zhang, W. Bai, J. Ren, W. Weng, H. Lin, Z. Zhang, H. Peng, *J. Mater. Chem. A* **2014**, *2*, 11054.
- [46] 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.
- [47] Y.-H. Zhu, S. Yuan, D. Bao, Y.-B. Yin, H.-X. Zhong, X.-B. Zhang, J.-M. Yan, Q. Jiang, *Adv. Mater.* **2017**, *29*, 1603719.
- [48] S. Yuan, X.-L. Huang, D.-L. Ma, H.-G. Wang, F.-Z. Meng, X.-B. Zhang, *Adv. Mater.* **2014**, *26*, 2273.
- [49] Y.-H. Zhu, X. Yang, D. Bao, X.-F. Bie, T. Sun, S. Wang, Y.-S. Jiang, X.-B. Zhang, J.-M. Yan, Q. Jiang, *Joule* **2018**, *2*, 736.
- [50] Z. Jian, Z. Xing, C. Bommier, Z. Li, X. Ji, *Adv. Energy Mater.* **2016**, *6*, 1501874.
- [51] Z. Guo, Y. Zhao, Y. Ding, X. Dong, L. Chen, J. Cao, C. Wang, Y. Xia, H. Peng, Y. Wang, *Chem* **2017**, *3*, 348.
- [52] D. Bin, F. Wang, A. G. Tamirat, L. Suo, Y. Wang, C. Wang, Y. Xia, *Adv. Energy Mater.* **2018**, *8*, 1703008.
- [53] H. Kim, J. Hong, K. Y. Park, H. Kim, S. W. Kim, K. Kang, *Chem. Rev.* **2014**, *114*, 11788.
- [54] M. Song, H. Tan, D. Chao, H. J. Fan, *Adv. Funct. Mater.* **2018**, *28*, 1802564.
- [55] A. Konarov, N. Voronina, J. H. Jo, Z. Bakenov, Y. K. Sun, S. T. Myung, *ACS Energy Lett.* **2018**, *3*, 2620.
- [56] G. Fang, J. Zhou, A. Pan, S. Liang, *ACS Energy Lett.* **2018**, *3*, 2480.
- [57] T. R. Juran, J. Young, M. Smeu, *J. Phys. Chem. C* **2018**, *122*, 8788.
- [58] R. Renuka, S. Ramamurthy, *J. Power Sources* **2000**, *87*, 144.
- [59] M. Minakshi, M. Blackford, M. Ionescu, *J. Alloys Compd.* **2011**, *509*, 5974.
- [60] K. Wang, X. Zhang, J. Han, X. Zhang, X. Sun, C. Li, W. Liu, Q. Li, Y. Ma, *ACS Appl. Mater. Interfaces* **2018**, *10*, 24573.

- [61] F. Wan, L. Zhang, X. Wang, S. Bi, Z. Niu, J. Chen, *Adv. Funct. Mater.* **2018**, *28*, 1804975.
- [62] Z. Wang, Z. Ruan, Z. Liu, Y. Wang, Z. Tang, H. Li, M. Zhu, T. F. Hung, J. Liu, Z. Shi, C. Zhi, *J. Mater. Chem. A* **2018**, *6*, 8549.
- [63] H. Li, Z. Liu, G. Liang, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Tang, Y. Wang, B. Li, C. Zhi, *ACS Nano* **2018**, *12*, 3140.
- [64] J.-S. Lee, S. Tai Kim, R. Cao, N.-S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34.
- [65] P. Tan, B. Chen, H. Xu, H. Zhang, W. Cai, M. Ni, M. Liu, Z. Shao, *Energy Environ. Sci.* **2017**, *10*, 2056.
- [66] Y. Li, H. Dai, *Chem. Soc. Rev.* **2014**, *43*, 5257.
- [67] J. Pan, Y. Y. Xu, H. Yang, Z. Dong, H. Liu, B. Y. Xia, *Adv. Sci.* **2018**, *5*, 1700691.
- [68] J. Fu, J. Zhang, X. Song, H. Zarrin, X. Tian, J. Qiao, L. Rasen, K. Li, Z. Chen, *Energy Environ. Sci.* **2016**, *9*, 663.
- [69] Q. Liu, Y. Wang, L. Dai, J. Yao, *Adv. Mater.* **2016**, *28*, 3000.
- [70] S. Qu, Z. Song, J. Liu, Y. Li, Y. Kou, C. Ma, X. Han, Y. Deng, N. Zhao, W. Hu, C. Zhong, *Nano Energy* **2017**, *39*, 101.
- [71] F. Cheng, J. Chen, *Chem. Soc. Rev.* **2012**, *41*, 2172.
- [72] D. Ji, L. Fan, L. Li, N. Mao, X. Qin, S. Peng, S. Ramakrishna, *Carbon* **2019**, *142*, 379.
- [73] L. Yang, L. Shi, D. Wang, Y. Lv, D. Cao, *Nano Energy* **2018**, *50*, 691.
- [74] H.-F. Wang, C. Tang, B. Wang, B.-Q. Li, X. Cui, Q. Zhang, *Energy Storage Mater.* **2018**, *15*, 124.
- [75] Y. Li, C. Zhong, J. Liu, X. Zeng, S. Qu, X. Han, Y. Deng, W. Hu, J. Lu, *Adv. Mater.* **2018**, *30*, 1703657.
- [76] M. Yu, Z. Wang, C. Hou, Z. Wang, C. Liang, C. Zhao, Y. Tong, X. Lu, S. Yang, *Adv. Mater.* **2017**, *29*, 1602868.
- [77] J. Fu, F. M. Hassan, J. Li, D. U. Lee, A. R. Ghannoum, G. Lui, Md. A. Hoque, Z. Chen, *Adv. Mater.* **2016**, *28*, 6421.
- [78] F. Meng, H. Zhong, D. Bao, J. Yan, X. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 10226.
- [79] C. Guan, A. Sumboja, W. Zang, Y. Qian, H. Zhang, X. Liu, Z. Liu, D. Zhao, S. J. Pennycook, J. Wang, *Energy Storage Mater.* **2019**, *16*, 243.
- [80] H.-G. Wang, S. Yuan, D.-L. Ma, X.-B. Zhang, J.-M. Yan, *Energy Environ. Sci.* **2015**, *8*, 1660.
- [81] X. Wang, Y. Li, T. Jin, J. Meng, L. Jiao, M. Zhu, J. Chen, *Nano Lett.* **2017**, *17*, 7989.
- [82] B. Li, X. Ge, F. W. Thomas Goh, T. S. Andy Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu, Y. Zong, *Nanoscale* **2015**, *7*, 1830.
- [83] D. Ji, L. Fan, L. Li, S. Peng, D. Yu, J. Song, S. Ramakrishna, S. Guo, *Adv. Mater.* **2019**, *31*, 1808267.
- [84] A. R. Mainar, O. Leonet, M. Bengoechea, I. Boyano, I. de Meatza, A. Kvasha, A. Guerfi, J. A. Blazquez, *Int. J. Energy Res.* **2016**, *40*, 1032.
- [85] J. Zhang, J. Fu, X. Song, G. Jiang, H. Zarrin, P. Xu, K. Li, A. Yu, Z. Chen, *Adv. Energy Mater.* **2016**, *6*, 1600476.
- [86] J. Fu, Z. P. Cano, M. G. Park, A. Yu, M. Fowler, Z. Chen, *Adv. Mater.* **2017**, *29*, 1604685.
- [87] A. Sumboja, M. Lübke, Y. Wang, T. An, Y. Zong, Z. Liu, *Adv. Energy Mater.* **2017**, *7*, 1700927.
- [88] C. Lin, S. i S. Shinde, Y. Wang, Y. Sun, S. Chen, H. Zhang, X. Li, J.-H. Lee, *Sustainable Energy Fuels* **2017**, *1*, 1909.
- [89] X. Chen, B. Liu, C. Zhong, Z. Liu, J. Liu, L. Ma, Y. Deng, X. Han, T. Wu, W. Hu, J. Lu, *Adv. Energy Mater.* **2017**, *7*, 1700779.
- [90] S. Zeng, H. Chen, H. Wang, X. Tong, M. Chen, J. Di, Q. Li, *Adv. Mater.* **2016**, *28*, 6421.
- [91] Z. Pei, Y. Huang, Z. Tang, L. Ma, Z. Liu, Q. Xue, Z. Wang, H. Li, Y. Chen, C. Zhi, *Energy Storage Mater.* **2019**, *20*, 234.
- [92] X. Fan, J. Liu, Z. Song, X. Han, Y. Deng, C. Zhong, W. Hu, *Nano Energy* **2019**, *56*, 454.
- [93] Y. Xu, Y. Zhang, Z. Guo, J. Ren, Y. Wang, H. Peng, *Angew. Chem., Int. Ed.* **2015**, *54*, 15390.
- [94] J. Park, M. Park, G. Nam, J.-S. Lee, J. Cho, *Adv. Mater.* **2015**, *27*, 1396.
- [95] X. Chen, C. Zhong, B. Liu, Z. Liu, X. Bi, N. Zhao, X. Han, Y. Deng, J. Lu, W. Hu, *Small* **2018**, *14*, 1702987.
- [96] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2012**, *11*, 19.
- [97] F. Li, T. Zhang, H. Zhou, *Energy Environ. Sci.* **2013**, *6*, 1125.
- [98] L. Ma, T. Yu, E. Tzoganakis, K. Amine, T. Wu, Z. Chen, J. Lu, *Adv. Energy Mater.* **2018**, *8*, 1800348.
- [99] J.-S. Lee, S. T. Kim, R. Cao, N.-S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34.
- [100] Z.-W. Chang, J.-J. Xu, Q.-C. Liu, L. Li, X.-B. Zhang, *Adv. Energy Mater.* **2015**, *5*, 1500633.
- [101] T. Liu, Q.-C. Liu, J.-J. Xu, X.-B. Zhang, *Small* **2016**, *12*, 3101.
- [102] Y.-B. Yin, X.-Y. Yang, Z.-W. Chang, Y.-H. Zhu, T. Liu, J.-M. Yan, Q. Jiang, *Adv. Mater.* **2018**, *30*, 1703791.
- [103] J. K. Papp, J. D. Forster, C. M. Burke, H. W. Kim, A. C. Luntz, R. M. Shelby, J. J. Urban, B. D. McCloskey, *J. Phys. Chem. Lett.* **2017**, *8*, 1169.
- [104] Q.-C. Liu, J.-J. Xu, D. Xu, X.-B. Zhang, *Nat. Commun.* **2015**, *6*, 7892.
- [105] S. Pan, H. Lin, J. Deng, P. Chen, X. Chen, Z. Yang, H. Peng, *Adv. Energy Mater.* **2015**, *5*, 1401438.
- [106] Y. Zhang, L. Wang, Z. Guo, Y. Xu, Y. Wang, H. Peng, *Angew. Chem., Int. Ed.* **2016**, *55*, 4487.
- [107] X.-Y. Yang, J.-J. Xu, Z.-W. Chang, D. Bao, Y.-B. Yin, T. Liu, J.-M. Yan, D.-P. Liu, Y. Zhang, X.-B. Zhang, *Adv. Energy Mater.* **2018**, *8*, 1702242.
- [108] X. Lin, Q. Kang, Z. Zhang, R. Liu, Y. Li, Z. Huang, X. Feng, Y. Ma, W. Huang, *J. Mater. Chem. A* **2017**, *5*, 3638.
- [109] B. D. McCloskey, A. Speidel, R. Scheffler, D. C. Miller, V. Viswanathan, J. S. Hummelshoj, J. K. Norkov, A. C. Luntz, *J. Phys. Chem. Lett.* **2012**, *3*, 997.
- [110] M. M. O. Thotiyil, S. A. Freunberger, Z. Peng, P. G. Bruce, *J. Am. Chem. Soc.* **2013**, *135*, 494.
- [111] D. M. Itkis, D. A. Semenenko, E. Y. Kataev, A. I. Belova, V. S. Neudachina, A. P. Sirotnina, M. Hävecker, D. Teschner, A. Knop-Gericke, P. Dudin, A. Barinov, E. A. Goodilin, Y. Shao-Horn, L. V. Yashina, *Nano Lett.* **2013**, *13*, 4697.
- [112] J. Xu, Z. Chang, Y. Yin, X. Zhang, *ACS Cent. Sci.* **2017**, *3*, 598.
- [113] Q. Liu, Z. Chang, Z. Li, X. Zhang, *Small Methods* **2018**, *2*, 1700231.
- [114] H. Jung, J. Hassoun, J. Park, Y. Sun, B. Scrosati, *Nat. Chem.* **2012**, *4*, 579.
- [115] C. J. Allen, J. Hwang, R. Kautz, S. Mukerjee, E. J. Plichta, M. A. Hendrickson, K. M. Abraham, *J. Phys. Chem. C* **2012**, *116*, 20755.
- [116] G. A. Elia, J. Hassoun, W. J. Kwak, Y. K. Sun, B. Scrosati, F. Mueller, D. Bresser, S. Passerini, P. Oberhumer, N. Tsiouvaras, J. Reiter, *Nano Lett.* **2014**, *14*, 6572.
- [117] L. Wang, J. Pan, Y. Zhang, X. Cheng, L. Liu, H. Peng, *Adv. Mater.* **2018**, *30*, 1704378.
- [118] N. Li, D. Xu, D. Bao, J. Ma, X. Zhang, *Chin. J. Catal.* **2016**, *37*, 1172.
- [119] Y. Li, J. Zhou, T. Zhang, T. Wang, X. Li, Y. Jia, J. Cheng, Q. Guan, E. Liu, H. Peng, B. Wang, *Adv. Funct. Mater.* **2019**, *29*, 1808117.
- [120] J. Zhou, X. Li, C. Yang, Y. Li, K. Guo, J. Cheng, D. Yuan, C. Song, J. Lu, B. Wang, *Adv. Mater.* **2019**, *31*, 1804439.
- [121] X. Fang, W. Weng, J. Ren, H. Peng, *Adv. Mater.* **2016**, *28*, 491.
- [122] Y. Xu, Y. Zhao, J. Ren, Y. Zhang, H. Peng, *Angew. Chem., Int. Ed.* **2016**, *55*, 7979.