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Designing Flexible Lithium-Ion Batteries by Structural Engineering

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ABSTRACT: **Flexible lithium-ion batteries (LIBs) can be seamlessly integrated into flexible devices, such as flexible displays, wearable devices, and smart cards, to provide power for steady operation under mechanical deformation. An ideal flexible battery should have high flexibility, high energy density, and high power density simultaneously, which are often in conflict with each other. In this Perspective, we analyze the flexible batteries based on structural designs from both the component level and device level. Recent progress in flexible LIBs, including advances in porous structures for battery components, superslim designs, topological architectures, and battery structures with decoupling concepts, is reviewed. In the end, perspectives on the future of flexible batteries are presented and discussed.**

Interests in flexible devices have surged in the past several decades, in areas such as flexible displays,[1] active radio frequency identification tags,[2] wearable health devices,[3] and flexible solar panels.[4] The application of these flexible devices will remarkably advance sustainability, health, security, and connectivity of humanity. With their rapid developments, it is desirable to develop flexible batteries that can continuously provide and store energy for these devices, even under the high level of mechanical deformation. Such flexibility is difficult to achieve in conventional battery designs, where multiple layers of components are stacked together and sealed tightly inside of a container. Even slight flexing can cause delamination and damage to active materials inside and consequential battery failures.

> High energy density, high flexibility, and dynamically stable power output should be achieved simultaneously in flexible batteries.

Table 1. Maximum Strain in Flexible Devices and Affordable Strain in Metal Foils in Batteries[5−7]

flexible device or material	target bending radius (mm)	thickness (mm)	nominal strain level or tensile strain
watch belts[5]	20	2	5.0%
flexible phones[5]	30	3	5.0%
foldable phones[6]	∼3	3	50%
flexible TVs[6]	30	2.5	4.2%
Al[7]		0.01	2.7% for once; 0.6% for 100 000 times

The requirement on flexibility varies from application to application, but it is typically well beyond the reversible strain of battery components (Table 1).[5,6] For example, a flexible battery in cell phones (e.g., 3 mm in thickness) needs to suffer a nominal strain of ∼5% when bent to a radius of 30 mm. In contrast, the tensile fracture strains of aluminum and copper foils are roughly 2.7 and 4.5%, respectively, let alone that their yield strains are only 0.9 and 1.2%, respectively.[7,8] Therefore, novel materials and designs are required to render batteries flexible. Otherwise, battery components will be damaged, which not only causes malfunctioning but may also result in thermal runaway and safety hazards. On the other side, it is also critical that the energy density is not remarkably compromised due to the deployment of these novel materials and designs because volume and weight are top considerations in portable devices mentioned above. Unfortunately, high flexibility and high energy density trade off with each other in general because high flexibility typically needs the introduction of redundancy in volume to release strain in batteries.

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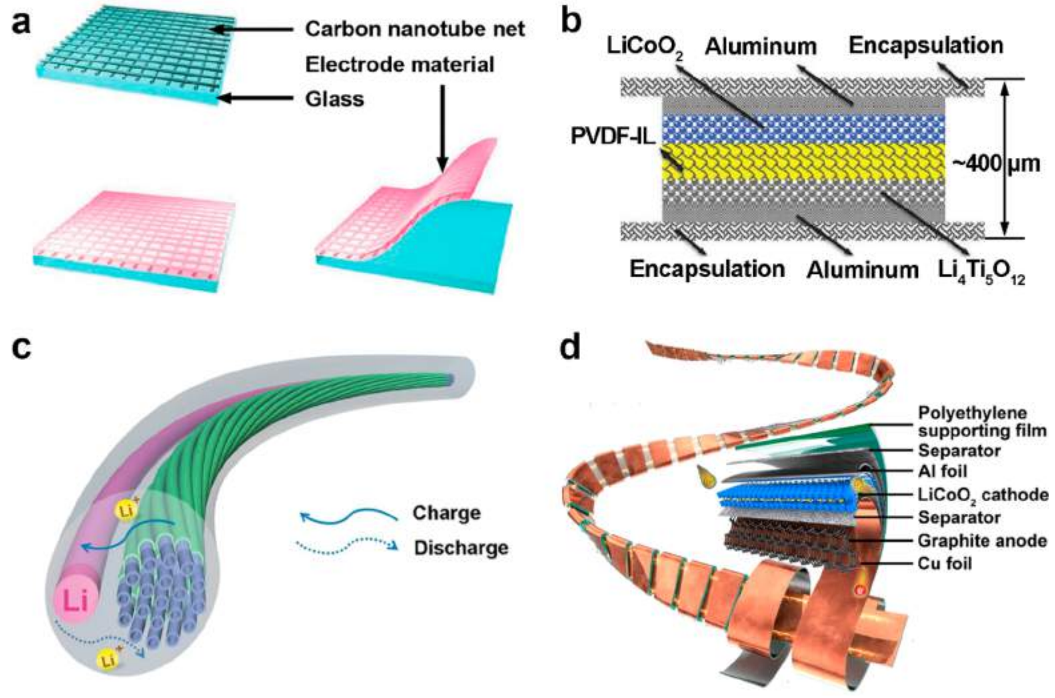

Figure 1. Summary of common strategies to render batteries flexible. (a) Inclusion of porous structure. The schematic shows an example with superaligned carbon nanotube (CNT) films that function as lightweight and thin current collectors. Adapted with permission from ref 9. Copyright 2012 John Wiley Sons, Inc. (b) Superslim structure. The optical image shows the schematic of a flexible thin-film battery based on solid-like ionic liquid−polymer electrolytes. Reprinted with permission from ref 10. Copyright 2016 Elsevier. (c) Topological design. The schematic illustrates a half-cell based on the aligned multiwalled carbon nanotube/Si composite fibers as the working electrode with a lithium wire as both the counter and reference electrode. Adapted with permission from ref 11. Copyright 2012 John Wiley Sons, Inc. (d) Decoupling energy storage and flexibility. The schematic shows a spine-like battery to decouple the energy storage part and the flexible component.

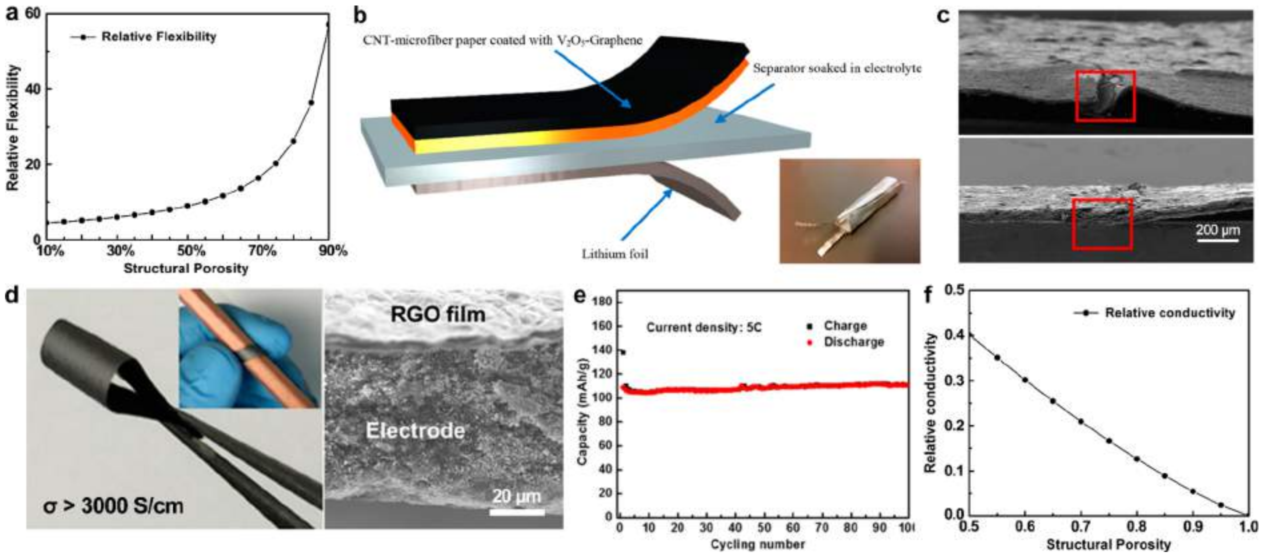

Figure 2. Porous current collectors for flexible LIBs. (a) Relative flexibility of the porous structure as a function of porosity with respect to the solid material. (b) Schematics of a paper-based V_2O_5/Li cell; the inset of the image is a completely bent paper-based pouch cell. (c) Field emission scanning electron microscopy (FESEM) images of a hybrid V_2O_5/graphene electrode in (b) after a bending test. The upper one is the cross section of a conventional metallic substrate, and the lower one is a paper-based electrode. All electrodes were bent 90° 20 times. Adapted with permission from ref 28. Copyright 2018 American Chemical Society. (d) Left: The high-temperature, Joule-heated RGO is mechanically flexible. Right: SEM image of a $LiFePO_4$ composite cathode coated on a RGO current collector, showing excellent substrate/electrode contact. (e) Cycling performance of a $LiFePO_4$ electrode with a RGO film current collector at 5C. Adapted with permission from ref 29. Copyright 2016 American Chemical Society. (f) Relative conductivity of metal foam as a function of porosity with respect to the intrinsic conductivity.

Besides high flexibility and high energy density simultaneously, another critical challenge for flexible batteries is the dynamic stability of power output during deformation. This requires the battery impedance to change as little as possible in dynamic bending. Practically the resulting change in overpotential should be less than 100 mV at operating currents, or roughly, the cell impedance should not be beyond doubled under mechanical deformation. In our experience, the major increase in impedance arises from deteriorated contact at various interfaces, such as the active material/metal substrate and active material/carbon black. Therefore, the battery should be tightly packed to enable intimate contact at these interfaces. However, this could compromise flexibility at the same time due to less room for flexing.

To address these challenges, various strategies have been reported in recent years. These reports can be categorized into the following four strategies: as illustrated in Figure 1, (1) inclusion of porous structure as deformable elements for current collectors, electrodes, separators, etc. (Figure 1a),[9] (2) superslim battery structure, such as a single thin layer of cathode/separator/anode stack (Figure 1b),[10] (3) topological designs to render lithium-ion batteries (LIBs) flexible, including wire-like and origami/kirigami structures (Figure 1c),[11] and (4) decoupling flexibility and energy storage components, such as spine-like batteries (Figure 1d).[12] Due to limits in the length, this Perspective will focus on only LIBs, which are widely used in state-of-the-art electronics and wearable devices. It should be born in mind that these strategies can also be applied to other kinds of batteries, such as Na-ion batteries, Li–S batteries, and other chemistries.[13−17]

In this Perspective, we will review some recent progress on these strategies, which can effectively render LIBs flexible. Meanwhile, we will discuss the fundamental science behind. For example, how do the flexibility and conductivity depend on structural porosity? How does energy density and flexibility depend on cell thickness? These models also provide guidance on the advantages and disadvantages of designs above, such as the cost of the superslim structure and composite substrates. At last, our perspectives on future trends are presented. This Perspective will only focus on flexible batteries, but not stretchable ones, which are well documented in other nice-written reviews.[18−20]

Porous structures have been widely used in battery components to dissipate strain generated when battery devices undergo bending and twisting. The fundamental mechanism is that the bending stiffness is lower for porous structures, which are hence more flexible than corresponding solid structures. Here, the relative flexibility α of porous structures is characterized by the bending stiffness ratio of the solid structure B_b to the porous structure B_p with the porosity ρ:[21]

$$\alpha = \frac{B_b}{B_p(\rho)} = \left(\frac{2(1+\sqrt{2})^2}{15} \frac{5\pi + 3(1-\rho)(1+\sqrt{2})^3}{25\pi + 7(1-\rho)(1+\sqrt{2})^3} (1-\rho) \right)^{-1} \tag{1}$$

As shown in Figure 2a, the flexibility increases exponentially with higher structural porosity. Quantitatively, the bending stiffness of the structure with porosity $\rho = 0.5$ is only 12.0% of that for pure solid with the same thickness, and thus, the stress in such a porous structure can be reduced by 88% when those structures are subjected to a static bending configuration with the same radius. Therefore, the adoption of porous material structures as battery components can render the whole battery device more flexible. In the following subsections, advances of using porous structures in substrates, electrodes, and separators/electrolytes will be discussed in sequence.

Standard substrates in Li-ion batteries are Cu and Al foils. Although they are flexible, it is difficult for them to survive either bending down to a small diameter (e.g., < 2 mm) or with repeated folding up to thousands of times due to mechanical fatigue. As good stress mitigators, porous structures, in which the pores can provide space to release various kinds of stresses, are employed as the current collector in flexible LIBs. These porous structures are typically made of conductive interconnected networks of foams/sponges or an interlocked network of fabric nets. Both the net-like (e.g., CNT paper)[22] and foam-like structures (e.g., 3D metal-based foam)[23] provide high flexibility, light weight, and high surface area to support active materials, which can also be produced at the industrial scale. The typical materials used in porous current collectors include carbon materials (nanotubes,[9] nanofibers,[24] and graphene[25]), metals,[26] and conductive polymers.[27]

This Perspective discusses structural design principles and strategies in flexible lithium-ion batteries. Fundamental mechanics and trade-off among various factors are discussed.

How to create a stable network of current collectors is important for flexible batteries. Recently, an interconnected CNT paper was developed as a flexible current collector, which can support V_2O_5/graphene hybrid active materials to achieve ultrahigh capacity (Figure 2b).[28] This flexible net-like substrate was fabricated by depositing single-wall CNTs over wood microfibers through a layer-by-layer self-assembly process. The porous structure of V_2O_5/ graphene on the softwood microfibers was demonstrated to be intact after bending tests, while the active materials were detached from the conventional aluminum current collector (Figure 2c). Although the layer-by-layer (16 layers) fabrication method provides a solution to overcome intrinsic conductive defects in wood nanofibers, the complex process with multiple steps may limit its practical applications. Moreover, Hu et al. also reported a highly conductive porous film of reduced graphene oxide (RGO) having conductivity up to 3112 S/cm (Figure 2d).[29] This porous RGO film was assembled into LIBs as current collectors, and no decay in specific capacity was observed during 100 charging/discharging cycles at 5C.

Although benefiting the flexibility of the substrate, porous structures may sacrifice the conductivity of current collectors compared to metal current collectors. Take the metal foam with interconnected open pores and the porosity of ρ as an example. The normalized electrical conductivity $\tilde{\sigma}$, defined as the ratio between the electrical conductivity of the foam and that of the corresponding solid material, can be analytically evaluated as[30]

$$\tilde{\sigma} = \frac{1}{3}[(1-\rho) + 2(1-\rho)^{3/2}] \tag{2}$$

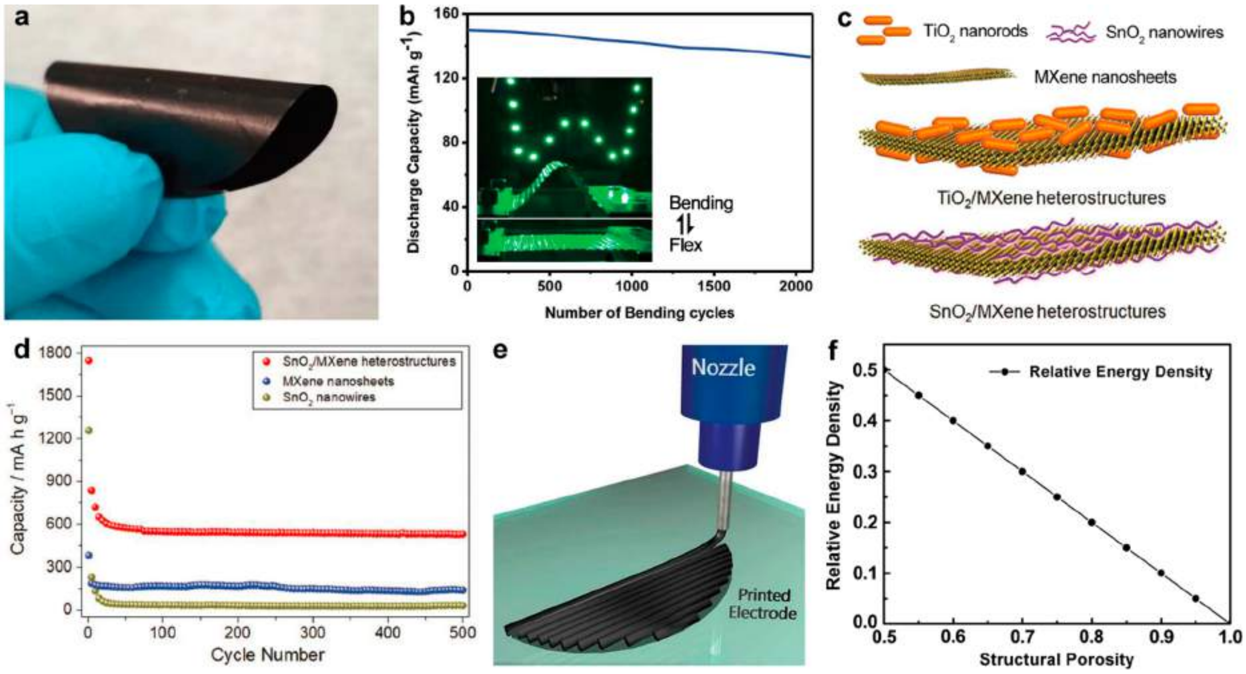

Figure 3. Porous electrodes for flexible LIBs. (a) Excellent flexibility of a PDHBQS/SWCNTs film. (b) Discharge capacity vs cycle number of the carbonyl compound-based flexible LIB. The inset shows the flexed configuration and the flat state of the carbonyl compound-based flexible LIB. Adapted with permission from ref 34. Copyright 2017 John Wiley Sons, Inc. (c) Schematic diagram for the simple self-assembly of TMO nanostructures, including TiO_2 nanorods and SnO_2 nanowires, on MXene nanosheets. (d) Cycling behaviors (current density = 1000 mA/g) of SnO_2/MXene heterostructures in (c). Adapted with permission from ref 35. Copyright 2018 John Wiley Sons, Inc. (e) Schematic illustration of the filamentary printing process. Reprinted with permission from ref 39. Copyright 2016 Royal Society of Chemistry. (f) Relative energy density of a battery using porous electrodes as a function of porosity, which shows that high porosity sacrifices energy density.

The conductivity for the porous foam with $\rho = 0.5$ is 40% of that for solid metal, and it further decreases with increased structural porosity, as shown in Figure 2f. Therefore, optimization of the porous current collector is critical for achieving flexibility and conductivity simultaneously in practical flexible LIBs.

By the conventional slurry coating-based fabrication, electrode materials can easily delaminate from substrates when the battery undergoes repetitive deformations. To alleviate interfacial stress between active particles and the substrate, porous active materials to be blended with the current collector network of porous substrates have been proposed to increase adhesion strength and areas. Various materials have been adopted in the interlocked composite for flexible LIBs, including soft inorganic materials (e.g., graphene,[31] aligned CNT,[9] carbon paper[22]), organic materials (e.g., thermoplastic polyurethane[32]), or organic−inorganic microstructures (e.g., intercalated metal−organic framework).[33] As an example of porous flexible electrodes, the composite cathode of the poly(2,5-dihydroxyl-1,4-benzoquinonyl sulfide) compound (PDHBQS) interlocked with single-wall carbon nanotubes (SWCNTs) has been fabricated for flexible LIBs (Figure 3a).[34] This design allows attractive charge storage capacity (discharge capacity of 182 mAh/g at 50 mA/g) as well as excellent rate performance (e.g., 75 mAh/g at 5000 mA/g). The dual function of SWCNTs as both a current collector and conductive additive is responsible for enhancing both the electrochemical performance and the mechanical stability. The as-fabricated flexible battery has a large footprint area (28 cm^2), and it can retain 88% of its initial discharge capacity after 2000 bending cycles (Figure 3b).

In addition, Xu and co-workers demonstrate the self-assembly of transition metal oxide (TMO) nanostructures of TiO_2 nanorods and SnO_2 nanowires on MXene (Ti_3C_2) nanosheets as a porous anode for flexible LIBs (Figure 3c).[35] The MXene nanosheets act not only as a conductive additive to facilitate electron and ion transport but also as a substrate to prevent the aggregation of the TMO nanostructures. The TMO nanostructures can prevent MXene nanosheets from being restacked during lithium insertion/extraction, thus enriching the interfacial contact and preserving the active areas. Due to the excellent synergy between the two building blocks, the TMO/MXene heterostructure exhibits superior cycling performance (Figure 3d). The role of MXene nanosheets as both the mechanical backbone and the ionic/electron conductors contributes to the flexibility of such electrodes, which has been also developed for other flexible energy storage.[36,37] In addition, flexible electrodes can be produced directly via 3D (Figure 3e),[38,39] stencil,[40] inkjet,[41] and aerosol jet printing[42] techniques, allowing scalable fabrication of flexible LIBs.

Although porous configurations for electrodes contribute to the flexibility of LIBs, the introduction of a void phase is at the expense of energy density. As shown in Figure 3f, the energy density for the electrode with a porosity larger than 0.6 would sacrifice 60% of the energy density compared with the dense one, and the significant drop in energy density could cause serious concerns in the operation time of electronic devices.

The porous structure of conventional polyethylene-based separators benefits not only ionic conductivity but also the mechanical compatibility between separators/electrodes. To enhance the safety, ceramic solid electrolytes are attractive for

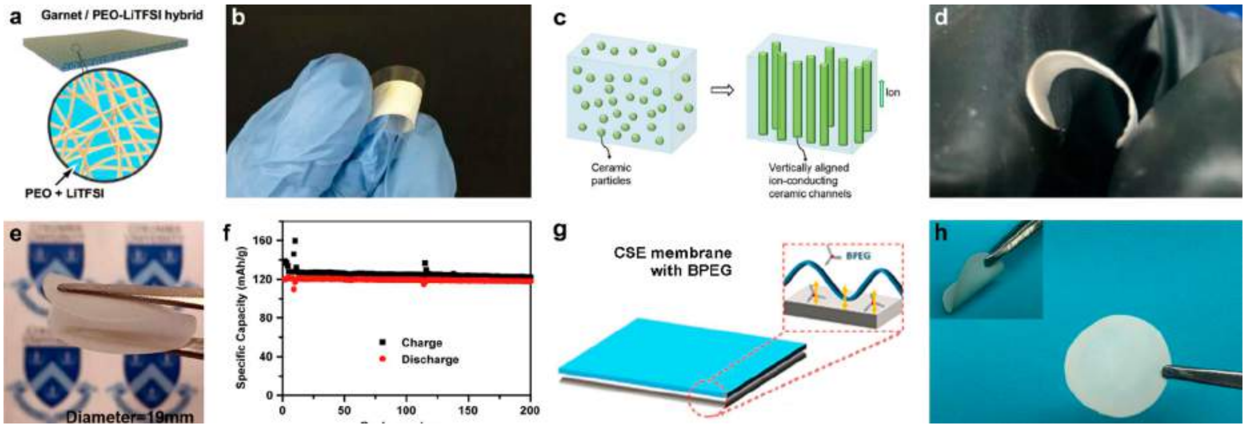

Figure 4. Porous solid electrolytes for flexible LIBs. (a) Schematic of a hybrid electrolyte with bacterial cellulose as an inexpensive, scalable, and efficient template. (b) Photo showing the flexibility of the hybrid electrolyte in (a). Adapted with permission from ref 43. Copyright 2018 John Wiley Sons, Inc. (c) Schematic of vertically aligned and connected ceramic channels for enhancing ionic conduction. (d) Camera image showing the flexibility of the composite film. Adapted with permission from ref 44. Copyright 2017 American Chemical Society. (e) Bent PVDF/palygorskite CSE showing excellent flexibility. (f) Cycling performance of Li($Ni_{1/3}Mn_{1/3}Co_{1/3}$)O_2/PVDF/5 wt % palygorskite CSE/Li cell (1C = 150 mA/g). Adapted with permission from ref 45. Copyright 2018 American Chemical Society. (g) Schematic illustration of a CSE membrane with boronized polyethylene glycol. (h) Optical image of a prepared CSE-boronized membrane. Adapted with permission from ref 46. Copyright 2017 John Wiley Sons, Inc.

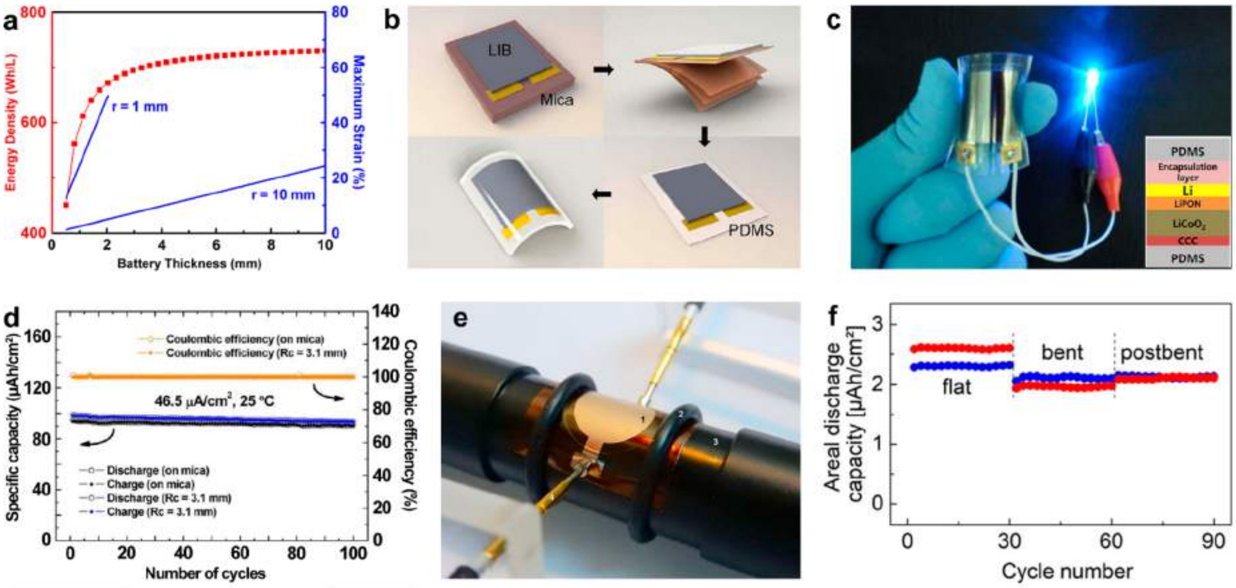

Figure 5. Designs of superslim flexible LIBs. (a) Trade-off between the energy density and the maximum strain of stacking cells as a function of the total thickness. Two different bending radii of r = 1 and 10 mm are used to calculate the maximum strain. The cell is considered as a uniform medium. (b) Schematic illustration of the process for fabricating bendable solid-state LIBs. (c) Photograph of the bendable solid-state LIB turning on a blue LED in the bent condition. The inset shows stacked layers in the flexible LIB. (d) Corresponding cycling performance and Coulombic efficiency of a flexible LIB bent down to R_c = 3.1 mm. Adapted with permission from ref 47. Copyright 2012 American Chemical Society. (e) Camera image of a thin-film all-solid-state LIB with the structure of LTO/LiPON/Li. (f) Performance of a thin-film all-solid-state cell at 2 μA (1C) in prebent, bent, and postbent conditions. The dashed line indicates the configuration change from flat to bent and back to flat. Adapted with permission from ref 48. Copyright 2018 Elsevier.

the next generation of batteries. However, incorporation of such rigid and fragile materials into flexible batteries is challenging the battery community. Recently, various designs of porous ceramic electrolytes embedded in the polymer matrix have been demonstrated as a viable solution.

Hu and co-workers developed a hybrid solid electrolyte of $Li_7La_3Zr_2O_{12}$ (LLZO) and poly(ethylene oxide)-based by exploiting bacterial cellulose as the template (Figure 4a).[43] With the soft but robust polymer matrix as the mechanical support, the interconnected porous LLZO network for transporting Li ions shows both a high ionic conductivity of 1.12 × 10^{-4} S cm^{-1} and excellent mechanical flexibility. Negligible impedance change has been measured for this composite solid electrolyte (CSE) undergoing bending (Figure 4b).

In addition, Yang et al. report a flexible CSE with vertically aligned columns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) nanoparticles by the ice templating process (Figure 4c). Its conductivity reaches 0.52 × 10^{-4} S/cm while maintaining flexibility (Figure 4d).[44] To further enhance the mechanical robustness of the

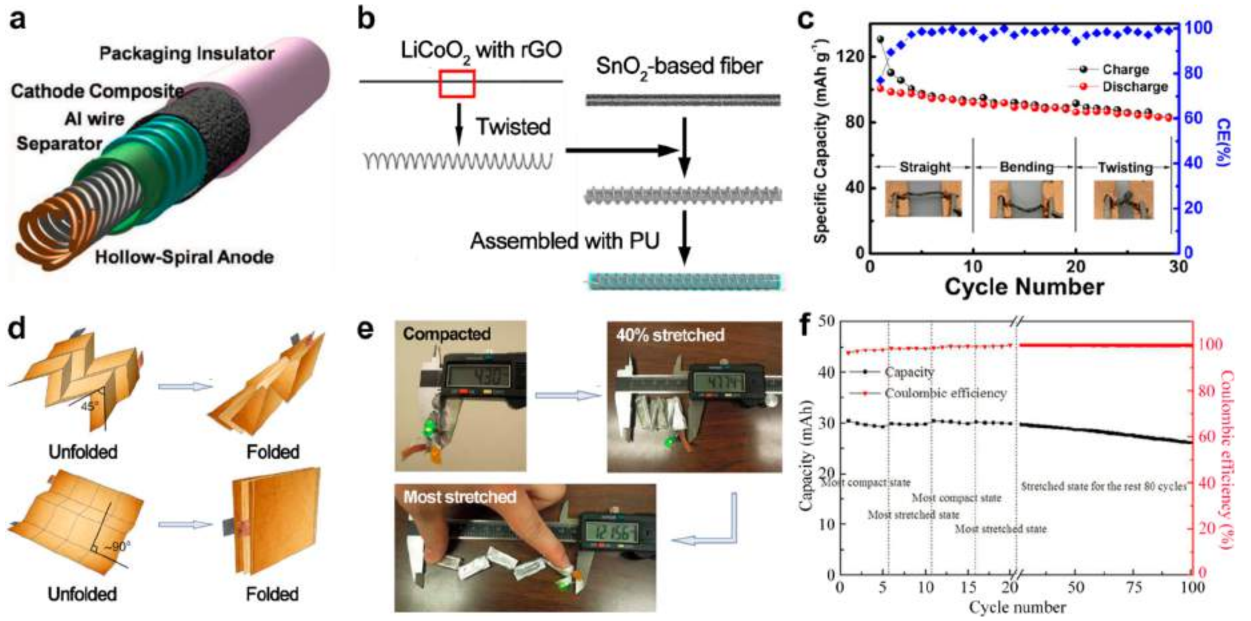

Figure 6. Various topological flexible LIB configurations. (a) Schematic illustration of the cable battery with a hollow-helix anode having multiple-helix structure. Adapted with permission from ref 50. Copyright 2012 John Wiley Sons, Inc. (b) Schematic diagram of manufacturing steps for fibrous electrodes and the assembly process of LIBs. (c) Cycling performance of a quasi-solid-state LIB at straight, bending, and twisting states. Adapted with permission from ref 53. Copyright 2018 Elsevier. (d) Two examples of origami LIBs using miura folding. Adapted with permission from ref 55. Copyright 2014 Nature Publishing Group. (e) Photograph of a kirigami LIB at different configurations. (f) Cell capacity and Coulombic efficiency as a function of cycle number for a C/3 charge/discharge rate. Adapted with permission from ref 56. Copyright 2015 Nature Publishing Group.

CSE, this group introduces palygorskite ($(Mg,Al)_2Si_4O_{10}(OH)$) nanowires as ceramic fillers.[45] The strong nanowire−polymer interaction and the cross-linking network of nanowires greatly improve both stiffness and toughness of the poly(vinylidene fluoride) (PVDF)-based polymer electrolyte, while the CSE film still shows excellent flexibility (Figure 4e). The fabricated $Li(NiCoMn)_{1/3}O_2$/Li cell can be cycled over 200 times at 0.3 C, with 97% capacity retention (Figure 4f). To address the issue of large interfacial resistance and mechanical compatibility between the solid electrolyte film and electrodes, Pan et al. propose the concept of "soft contact", which not only chemically enables homogeneous lithium plating/stripping on the lithium metal anode but also reduces the polarization effects (Figure 4g,h).[46]

Besides using porous structure for battery components, reducing battery thickness is a device-level design for flexible batteries. From the view of mechanics, the maximum strain ϵ in a slab is proportional to its thickness t, $\epsilon = t/2R$, where R is the bending radius, and the relationship is presented in Figure 5a. When the battery thickness is reduced to 0.5 mm and the bending radius is 20 mm, the maximum strain of 1.25% is comparable to tensile failure strain of the metals inside (e.g., 0.7% for Al and 1.2% for Cu). Further increasing the thickness will unavoidably damage components inside of a battery, even though larger thickness benefits higher energy density.

Various superslim LIBs have been demonstrated by companies. Panasonic Corporation developed a flexible LIB with a thickness of only 0.55 mm, which is suitable for applications in card-type and wearable devices. This rechargeable battery can retain its performance (over a capacity retention of 99%) even after being repeatedly bent to a radius of 25 mm or twisted to an angle of 25°.

Besides conventional liquid electrolyte-based LIBs, the superslim strategy can also render ceramic-based solid-state batteries flexible because ceramic films become flexible at ultralow thickness (e.g., <10 μm). For example, Lee et al. demonstrate a $LiCoO_2$ (5 μm)/lithium phosphorus oxynitride (LiPON) (2 μm)/Li flexible solid-state battery sandwiched between two PDMS packaging films (Figure 5b,c).[47] The flexible LIB can survive being bent down to a radius of 3.1 mm. This thin-film battery shows a reasonable capacity of 106 μAh/cm^2 and a capacity retention of 94.5% after 100 cycles (Figure 5d), even with a bending radius of R_c = 3.1 mm. The reason for such mechanical robustness is that the nominal strain in the battery is only ~10 μm/5 cm/2 = 0.01%, much less than the typical failure strain in ceramics (e.g., ~ 0.1%). The adoption of such a solid-state electrolyte also provides better safety compared to conventional liquid-based LIBs.

Recently Kun et al. also reported a facile flame spray pyrolysis-based method to fabricate a thin-layer solid-state battery of $Li_4Ti_5O_{12}$ (LTO)/LiPON/Li, supported by flexible polyimide substrates (Figure 5e).[48] Excellent capacity retention has been demonstrated as there is no capacity loss for 30 cycles at 2 μA (1C) in the flat state. Upon static bending, the capacity shows an obvious drop from 2.6 to 1.9 μAh/cm^2, which may arise from the contact failure from stress generated inside of the cell (Figure 5f). However, the cycling performance is still highly steady in the next 30 cycles.

The superslim design can remarkably enhance battery flexibility as the small thickness reduces strain inside. However, this is typically at the expense of energy density because a 70−100 μm thick laminated aluminum sheet layer is necessary for battery packing to avoid the permeation of O_2 and moisture. Therefore, as shown in Figure 5a, the energy density of batteries with a thickness less than 1 mm would be 20% lower than thick ones (e.g., 5 mm), with assumptions of common thickness for electrodes and separators (e.g., 60 μm for active materials, 10 μm for metal substrate, and 15 μm for

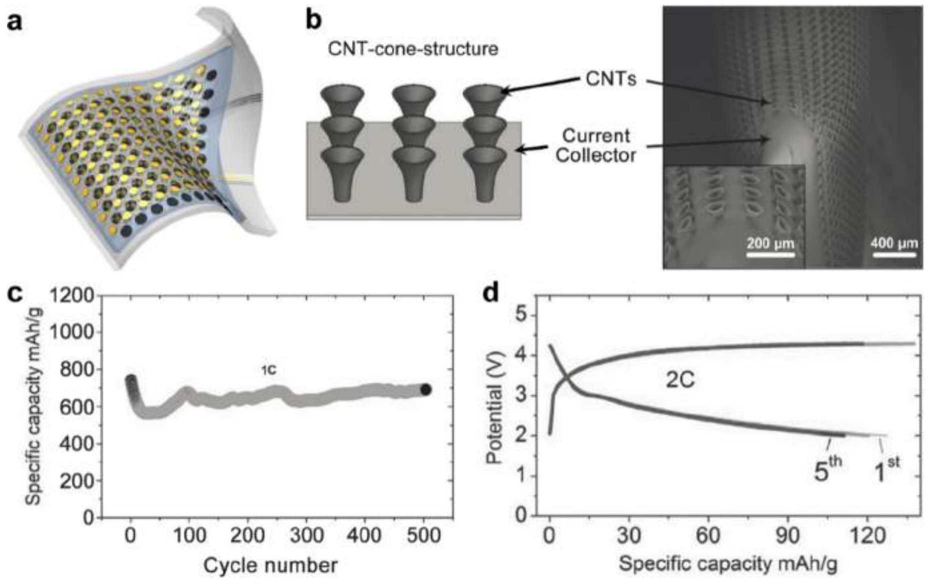

Figure 7. Battery fabricated with the strategy of decoupling flexibility and energy storage. (a) Schematic illustrating a battery with "self-similar" interconnect structures. Reprinted with permission from ref 57. Copyright 2013 Nature Publishing Group. (b) Left: Schematic of a transferred CNT cone polymer film. Right: SEM image of a bent CNT cone electrode. Scale bar: 400 μm. The inset shows the magnified SEM image. Scale bar: 200 μm. (c) Extended lifetime testing of the CNT cone electrodes at 1C rate for 500 cycles. (d) Charge/discharge curves of a corresponding full cell: iron oxide−CNT cones and LNCO−CNT cones at 2 C. Adapted with permission from ref 58. Copyright 2016 John Wiley Sons, Inc.

separators). For a single pair of $LiCoO_2$/graphite electrodes with cell thickness of 0.5 mm, the energy density is 475 Wh/L, only 63% of that at 3 mm thickness, the common thickness for batteries in cell phones. Such a drop in energy density may reduce the operation time of electronic devices.

Besides improving the flexibility of the material itself, an alternative approach to realizing flexible batteries is to design a battery architecture to reduce strain inside. The two strategies above for the flexible batteries use the same configuration as conventional prismatic/stacking cells. On the other side, it is also possible to redesign the battery architecture to address challenges in flexibility, such as wire-shaped,[49] cable-type,[50] wave-like,[51] miura pattern,[52] etc. These novel structures release constraints on battery configurations and thus can remarkably enhance cell flexibility. Meanwhile, reasonable electrochemical performances can still be maintained in these novel topological designs.

Wire-based battery architecture was first reported by Kim et al. in 2012, which can achieve extraordinary flexibility and reasonable electrochemical performance for flexible LIBs (Figure 6a).[50] They are capable of accommodating not only bending and flexing but also complex and extreme shape changes such as folding and twisting. Recently, Gao and co-workers designed and fabricated a wire-shaped flexible LIB by using a spring-like $LiCoO_2$/RGO cathode, a SnO_2-based anode, and a gel electrolyte (Figure 6b).[53] A self-healing polymer, carboxylated polyurethane (PU), has been applied as the packaging layer, which can recover the mechanical injuries and heal damage in the full cells by reconstructing broken interfaces with hydrogen bonds. The capacity is retained at 82.6 mAh/g after complex deformation (bending and twisting) and 50.1 mAh/g after the fifth healing process at a current density of 0.1 A/g, suggesting capacity retention of 82.2 and 50.3%, respectively (Figure 6c).

Besides wire-like structure, the art of paper folding has been applied to flexible batteries too. Using origami, a well-known scheme for paper folding,[54] compact deformable three-dimensional structures can be created from two-dimensional sheets through high degrees of folding along predefined creases (Figure 6d), and a high level of deformability can be achieved.[55] Soon afterward, the same group developed kirigami-based LIBs by combining folding and cutting.[56] It is shown that fracture due to cutting and folding is suppressed by plastic rolling, which provides kirigami LIBs' excellent and stable electrochemical and mechanical characteristics (Figure 6e). More than 85% capacity retention and Coulombic efficiency of 99.8% could be achieved after 100 charge−discharge cycles, while the maximum output power shows no noticeable decay over 3000 times battery deformation (Figure 6f).

Decoupling flexibility and energy storage enables flexibility, power performance, and energy density of flexible LIBs simultaneously. For the aforementioned flexible battery designs, the contact degradation between active materials and current collectors can still occur during the complex deformation process. The increasing overpotential due to contact degradation will reduce the capacity retention and Coulombic efficiency of the full cell. A potential solution is to redesign the battery architecture to decouple energy storage and flexibility.

Rogers and co-workers piled up and combined cell units with small size in series as "self-similar" geometries, which enable them flexible via the gap between different units (Figure 7a).[57] That means that this design induces the stress localized in the silicone elastomers instead of the electronic components, which smoothens oscillations in the output voltages under mechanical deformation. Following the step of Rogers, De Volder and co-workers demonstrated a hierarchical cone-shaped CNT structure, combining a slender base for stress reduction and a wide crown for particle loading (Figure 7b).[58] These microcones have slender trunks planted in a flexible lightweight current collector. In such a structure, the stress in

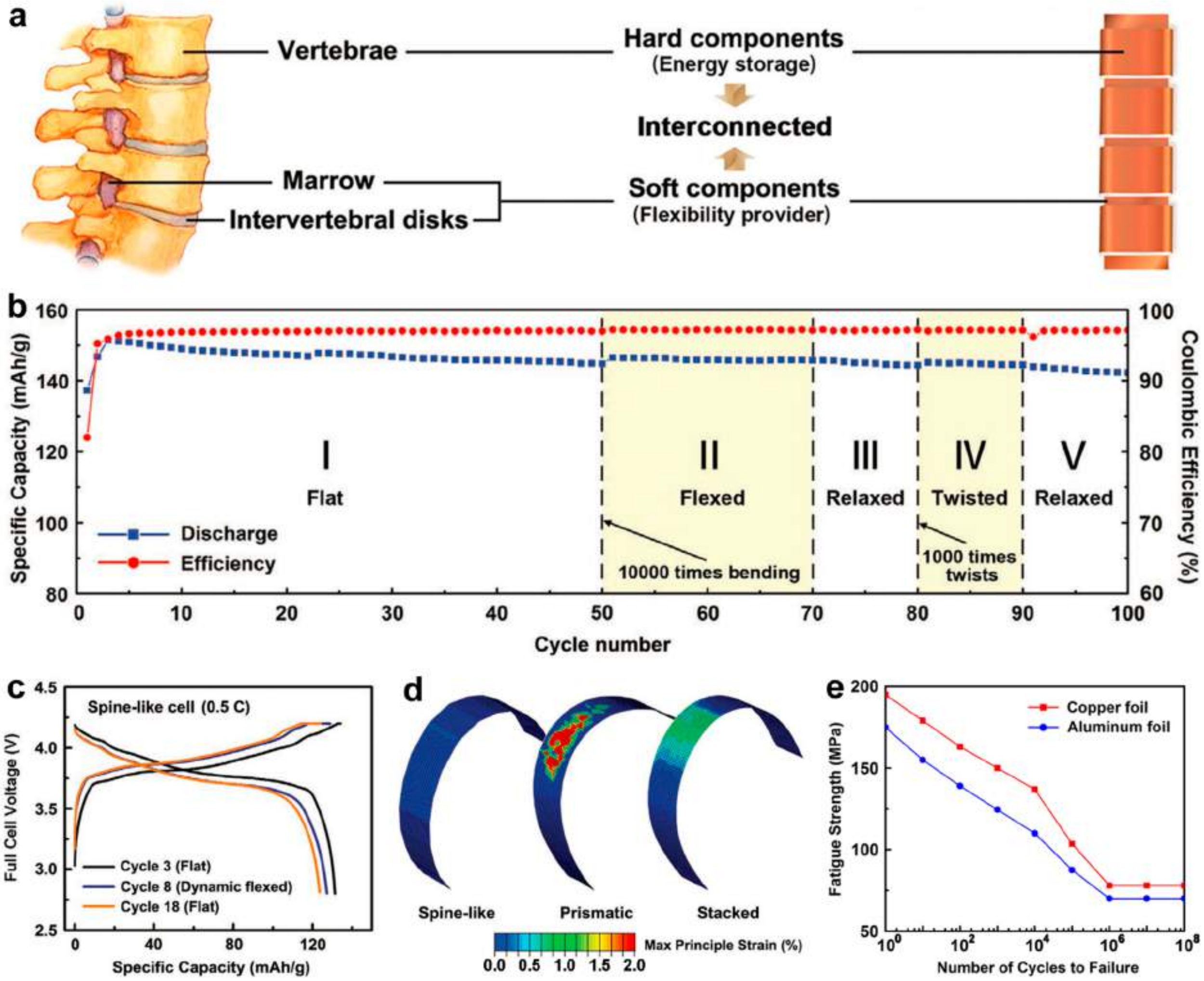

Figure 8. Bioinspired, spine-like, flexible LIBs. (a) Schematic illustration of bioinspired design of a spine-like battery. (b) Charge/discharge cycling test of the spine-like battery in different configurations at 0.2C (28 mA/g). (c) Galvanostatic charge−discharge curves for the 3rd, 8th, and 18th cycles of the spine-like cell with dynamic mechanical load. (d) Finite element analysis of the maximum principle strain in the spine-like battery, compared with the conventional prismatic and stacked structures. Adapted with permission from ref 12. Copyright 2018 John Wiley Sons, Inc. (e) Curves relating the stress level to the corresponding number of cycles to failure for both aluminum and copper foils.

the electrode is localized at the current collector and decoupled from the electroactive region (wide crowns), which remains unstressed during bending and exhibits an extremely high flexibility (300 μm radii). The cone electrodes are cycled 500 times at 1C rate with no appreciable change in the capacity (Figure 7c), and the as-fabricated Fe_2O_3/$LiNi_{0.8}Co_{0.2}O_2$ (LNCO) full cell delivers a reversible capacity of ∼120 mAh/g at 2C with a multitude of folded times (Figure 7d).

The designs above can successfully decouple energy storage and mechanical deformation. However, the relative percentage of area for energy storage is small (e.g., 20−50%) so that energy density will be compromised significantly. Recently, Qian et al. demonstrated a spine-inspired design that can increase the storage component to 80−90% of the total volume, so that high energy density can be achieved while maintaining high flexibility (Figure 8a).[12] In this design, the conventional graphite/separator/$LiCoO_2$/separator stacks have been wrapped around the backbone to form thick stacks for storing energy, while the unwound part interconnects all vertebra-like thick stacks together, which provides excellent flexibility for the whole device.

The energy density can reach 80−90% of that of conventional batteries, and a cell with 242 Wh/L is demonstrated with unoptimized electrode loading.[12] The capacity shows little decay after 10 000 bending times and 1000 twisted times (Figure 8b). More importantly, a dynamic mechanical load experiment was performed, and the full cell retains stable power output and cycling performance under continuous deformation (Figure 8c). Finally, numerical simulation results confirm that the spine-like structure sustained smaller strain (∼0.08%) compared with conventional prismatic cells (1.8%, Figure 8d). The excellent electrochemical and mechanical properties of this design are promising for wide applications in flexible and wearable electronics. In addition, this design can be further extended to foldable and stretchable batteries.[59,60]

In this strategy, as metal substrates are still used as the current collector, it is important to keep in mind that their tensile strength is a function of bending times. The stress for causing local structural damage is much less than the yield stress limit when material undergoes repeated loading. From the microscopic view, microcracks begin to form at the locations with concentrated stress such as the surface, interfaces of constituents, and grain boundaries. Upon the crack reaching a critical size during cyclic loading, it propagates suddenly and the structure is fractured. In real devices, the required cycles of applied loading could vary from 100 to 1000 times (e.g., large display) to ∼100 000 times (smart watches, foldable phones/pads) in devices' entire operating lives. Figure 8e shows the S−N relations between fatigue strength (S) and the corresponding cycle number to failure (N) for both copper and aluminum. Obviously, a higher level of stress leads to a smaller number of acceptable cycles. Take Cu as an example; when the number of cycles to failure is required to increase from 1 to 10 000 times, the maximum tensile stress (strain) has to be reduced from 196 MPa (3.0%) to 135 MPa (0.7%). In other words, it is equivalent to increasing the minimum bending radius 3 times. The nonproportionality between stress and strain is due to that the stress/strain is in the plastic regime, so that they are no longer linear. Such reduced tensile strength should be taken into account in designing flexible batteries so that the maximum strain will not exceed the limit.

In this Perspective, we show that turning the LIB flexible is a challenging topic, especially when high energy density, high power density, and being fatigue-proof over thousands and even hundreds of thousands of times are considered simultaneously. The strategies to realize flexible LIBs can be divided into four general approaches: porous structure, superslim cell, topological designs, and decoupling of energy and flexibility. In designing flexible batteries, the trade-off among energy density, power density, and flexibility should be carefully considered, so that a balanced performance can be achieved for practical applications.

In the future, we think the following two directions are important for high-performance flexible batteries: (1) fundamental understanding of underlying mechanics by simulations and experiments and (2) development of components with both high flexibility and electrochemical performance and system integration.

First, a deep understanding of mechanics in flexible batteries is needed. Although this Perspective analyzes strain inside of a flexible battery, it largely omits the particle ensemble nature of battery electrodes and corresponding mechanics inside, such as how sliding and moving of particles absorb stress and affect mechanical and electrochemical properties. This is also rarely studied in the literature but very important to fully understand mechanical processes in flexible LIBs and even conventional ones. More analytical, numerical, and experimental studies in this direction are urgently needed to understand strain distribution and weak spots inside. Such studies should also be coupled with electrochemistry to correlate mechanical behavior with battery performance. Such understanding will not only advance our fundamental knowledge in flexible batteries but also provide rational guide on designing practical devices.[59] Besides modeling, it is also critical to use advanced characterization tools to understand the fatigue behavior of flexible batteries, such as where the damage starts and how it propagates. Potential methods include synchrotron imaging[62] and magnetic resonance imaging (MRI).[63]

> Inclusion of porous structure, a superslim cell, topological design, and decoupling energy storage and flexibility are general strategies to render batteries flexible.

Second, material development plays a central role in advancing flexible batteries, including all components inside. For the current collector, it is critical to develop stable flexible substrates with high electronic conductivity and flexibility. The substrate should also not have a very high surface area; otherwise, side reaction with electrolyte will be promoted. For electrode materials, the major challenge is how to achieve high density and high mass loading while maintaining high flexibility and mechanical integrity. This is especially difficult for porous structures but less a challenge if energy storage and flexibility are decoupled. It should be noted that high mass loading on the order of 1−3 mAh/cm^2 is important for practical applications. Otherwise, the energy density will be severely compromised. The adhesion among different components is also critical as mechanical deformation is prone to cause delamination. Novel binders with high adhesion capability will be beneficial.

Table 2. Comparison of Electrochemical Performance in Literature Reports on Flexible LIBs[12,34,47,51,55,59,61]

design principle	electrode materials	specific capacity (mAh/g)	energy density (Wh/L)	cycle life	source
porous structure (porous electrode)	PDHBQS-SWCNTs/ Li foil	186 at 0.28C	n/a	88% capacity retention after 2000 bending cycles	ref 34
	LCO/LTO	130.7 at 0.1C	n/a	98% capacity retention after 150 bending cycles	ref 61
superslim	LCO/Li	n/a	2.2[a]	95% capacity retention after 100 electrochemical cycles	ref 47
	n/a	31.6 at 1C[a]	159.4[a]	99% capacity retention after 1000 bending cycles	Panasonic
topological designs	$LiCoO_2$ /graphite	14.4 at 1C[a]	43[a]	92% capacity retention after 2000 times of bending	ref 51
	LCO/LTO	85.5 at 0.15C	69.6[a]	84% capacity retention after 100 folding/ unfolding times	ref 55
decoupling energy and flexibility	$LiCoO_2$ /graphite	151 at 0.2C	242[a]	99% capacity retention after 10 000 bending cycles	ref 12
	$LiCoO_2$ /graphite	148.6 at 0.5C	275[a]	96% capacity retention after 100 electrochemical cycles	ref 59

[a]The calculation results are included with packaging materials.

Another important but often overlooked component is the packaging material. Metal cases, or metal foil sandwiched between plastics, are still mandatory for battery packaging to avoid penetration of moisture and air.[64] Therefore, even if electrodes, separators, and current collectors are all flexible, the packaging also needs to provide the same level of flexibility, which requires dealing with mechanical strength of metal inside to relieve strain in metal layers. This factor may make architectural design at the device level more favorable, so that the strain in metal layers can be well released.

Flexible LIBs are an exciting opportunity for developing next-generation energy storage devices and a multidisciplinary topic at the center of mechanics and electrochemistry. It is important to consider practical constraint in developing strategies to render batteries flexible. Exciting progress has been made during the last several decades, and commercial products have started to emerge in the market (Table 2). In the future, the development of novel materials, device architectures, and fabrication techniques will further enhance performance of flexible LIBs, especially for realizing a smaller bending radius, a higher energy density, and a larger number of bending cycles.

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