

A Super-Foldable Lithium-Ion Full Battery

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Developing foldable power sources with simple transport and storage remains a significant challenge and an urgent need for the advancement of nextgeneration wearable bioelectronics. In this study, super-foldable lithium-ion batteries are developed by integrating biomimetic methods, which effectively address the challenges of stress dispersion and mark a breakthrough in the field of super-foldable devices. A synchronous three-level biomimetic coupling technology is introduced and employed a strategy of radial compounding, gel-electrostatic molding, and temperature-programmed co-pyrolysis. This approach allows us to simultaneously prepare a super-foldable multi-level "lotus structure" cathode and a highly compatible super-foldable "peapods" structure anode. Remarkably, even after 500 000 cycles of repeated folding tests, the full battery maintains a high level of capacity stability, and the galvanostatic charge/discharge curves also exhibit a high degree of consistency. Furthermore, this battery can power an LED clock for over 2870 continuous minutes while undergoing in situ dynamic reciprocating folding, highlighting its substantial promise for practical applications. The super-foldable battery represents a full-chain innovation, extending from the super-foldable substrate to the super-foldable electrodes, and culminating in a super-foldable full battery.

1. Introduction

With the increasing demand for wearable bioelectronics, the foldability of small electronics has become an increasingly important feature.^[1–7] This includes the most sought-after foldable displays and foldable mobile phones.^[8] However, the current development of foldable electronics is still in its infancy. For instance,

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popular foldable phones currently on the market achieve foldability through a rotational axis but cannot arbitrarily deform or shrink the space.^[9] Energy storage devices, which serve as the foundation for a new generation of foldable electronic systems by providing power, predominantly consist of rigid structures. This limitation greatly impedes the practical development of foldable electronics. Typically, an energy storage device is composed of four components: electrodes, separators, electrolytes, and shells. To create a super-foldable energy storage device capable of withstanding numerous scatheless true folding cycles (Figure S1, Supporting Information), each component must endure the foldable operation without compromising the expected electrochemical performance of the device.[10-13]

In recent years, researchers have explored considerable advancements in foldable energy storage devices, aiming to develop devices that can withstand a large number of folding cycles, and

even achieve super-foldability for wearable devices.[3,8,14-16] To prepare a high-performance foldable energy storage device, it is essential to have suitable foldable electrode materials. Carbonbased electrode materials, known for their excellent flexibility, have attracted widespread attention.^[3,17-19] 1D carbon materials, such as carbon nanofibers, have served as foldable electrode materials.^[20,21] For example, foldable Ge_xO/ZnO/C nanofibers used as lithium-ion battery electrode materials can still be restored to their original state after three-layer folding.^[22] 2D graphene films are also employed as foldable electrode materials with multilayer porous graphene films able to withstand up to 2000 simple folds, delivering an area energy density of up to 30.8 µWh cm⁻² as a supercapacitor electrode.^[23] Moreover, to further enhance the specific capacity of the foldable electrodes, materials of different types are combined to form films used as foldable electrodes,^[24-27] such as the foldable composite film electrode composed of carbon nanofibers and graphene, which maintains stable resistivity after 400 folding cycles.^[28] The area energy density of these films as a capacitor electrode can reach 2.1 mWh cm⁻² at room temperature. However, the resistivity of the electrodes tends to increase with the number of folds, indicating irreversible damage to the electrode during multiple folds.

Researchers have actively explored the development of foldable batteries by incorporating LiCoO₂ and Li₂TiO₃ onto flexible substrates, such as graphene or carbon nanotubes (CNTs) membranes, creating foldable electrodes. These electrodes, when ADVANCED SCIENCE NEWS www.advancedsciencenews.com

combined with distinct structural designs like origami, have led to the assembly of foldable lithium-ion batteries.^[29–35] Despite these efforts, the foldability of such devices has been limited, achieving only a few dozen folding cycles. Similarly, foldable Li– O_2 batteries using "paper-ink" technology and foldable Li–S batteries, made by blending conductive carbon with sulfur powder into a film, have shown promising specific capacities but suffer from a 20% capacity loss after 100 bending cycles.^[33] In the field of foldable supercapacitors,^[15,36–40] devices assembled with spherical Ni(OH)₂ and graphite paper composite materials have experienced a 10% capacity reduction after just two folding cycles.^[41] Efforts to improve the foldability of capacitors, such as by incorporating CNTs into cellulose for the electrodes, have allowed for 1000 folding cycles but at a 40% loss in capacity.^[42]

The core challenge in achieving true super-foldability in these energy storage devices lies in managing the interaction between electrode/material construction and stress dispersion effectively. Moreover, three critical flaws have been identified: low conductivity, poor strength, and low effective loading, all of which hinder the development of durable energy storage devices.^[43–45] Successful components must not only manage stress effectively but also work in harmony with the entire assembly to ensure uniform stress distribution. This is crucial for maintaining the integrity and electrochemical stability of the materials during repeated folding.

This work introduces a novel "integrated electrode/substrate" approach that addresses the challenges faced by both the substrate and the electrode, bypassing the need for exploring super-foldable substrate materials. We move away from traditional biomimetic methods and, for the first time, adopt an advanced three-level biomimetic strategy that draws inspiration from silkworm cocoons, lotus roots, and peapods. Through a temperature-programmed co-pyrolysis method, we have developed highly foldable electrodes with excellent conductivity and strength, specifically, a super-foldable CNTs/LiFePO₄@Carbon nanofiber films (SCLiCF) cathode and a matching super-foldable CNTs/Fe₂P@Carbon nanofiber films (SCFeCF) anode.

Our breakthrough is the development of the first superfoldable lithium-ion full battery (SFLIB), which integrates biomimetic assembly of each component to overcome the stress dispersion issue during folding. Remarkably, after 500 000 true folding cycles, the battery's conductivity and capacity remain virtually unchanged, with its galvanostatic charge/discharge (GCD) curves showing consistent performance. Impressively, this super-foldable full battery can power an LED digital clock for over 2870 min during 30 000 true folding cycles. Overall, this represents a full-chain innovation process, from the development of super-foldable substrates and electrodes to the realization of super-foldable full batteries. Our multi-level integrated biomimetic strategies and co-coupling methods offer a promising path forward for the future of super-foldable electronic devices.

2. Results and Discussion

2.1. Biomimetic Design

To engineer the ideal SFLIB, a set of stringent criteria must be fulfilled, including 1) a rational stress-dispersion structure to accommodate folding, 2) high electrical conductivity to ensure efficient high flow, 3) optimal loading of active materials for maximum capacity, 4) prevention of active material loss or obstruction of foldability during folding, 5) maintenance of electrochemical stability throughout repeated folding. Meeting these requirements simultaneously presents a significant challenge. However, nature offers abundant inspiration for innovative solutions. In this context, we introduce a pioneering "three-in-one" biomimetic strategy to navigate these challenges (Figure 1).

Specifically, the process from cocoon spinning to reeling inspires an arbitrarily foldable "M" structure, a complete stress dispersion structure,^[47] suggesting a pathway to crafting superfoldable materials (Figure 1a). Additionally, the observation of fine tubular structures arranged radially in lotus stems (Figure 1b), which can provide a stress-buffering effect, demonstrates a natural mechanism for stress buffering, contributing to their remarkable flexibility. Furthermore, the "cabin" structure within a pod, facilitating uniform dispersion, particle fixation, and nutrient delivery (Figure 1c), offers a blueprint for integrating and protecting active materials within a flexible matrix. Employing gel electrospinning (Figure 1d), we synthesized a precursor composite fiber membrane that embodies these three biological insights in a single step (Figure 1e), closely mimicking the targeted biological processes and structures (Figure 1f). This biomimetic approach ensures the radial and uniform distribution of CNTs along the fibers, mimicking the inside structure of the lotus stems, thereby minimizing clustering, enhancing flexibility and conductivity. It also integrates active materials within the fibers in a way that echoes the "cabin" structure of pods, securing them against detachment and accommodating volume expansion during lithium-ion (Li⁺) cycling.

Moreover, coating the active particles with a polyacrylonitrile (PAN) precursor, which upon carbonization becomes highly conductive and porous, significantly improves electron/ion transfer rates. Through a gradient co-pyrolysis strategy, echoing the cocoon reeling process, we simultaneously produced selfsupporting super-foldable cathode (Figure 1g) and anode electrodes (Figure 1h). These electrodes are not only compatible but also maintain high specific capacities and exceptional foldability, overcoming the obstacles typically faced in designing and manufacturing high-quality super-foldable substrates (Figure 1i) and achieving a "one stone, three birds" outcome.

Ultimately, by applying principles of structural and stress coordination among all components and leveraging integrated biomimetic assembly, we have overcome the challenges of stress dispersion during folding. This culminated in the development of a SFLIB with superior electrochemical performance (Figure 1j). Remarkably, this battery demonstrates stable electrochemical output through a vast number of dynamic true folding cycles at any angle (Figure 1k,l), heralding a new era for foldable electronics and wearable devices (Figure 1m).

2.2. Preparation, Structures, and Performances Characterization

The synthesis of super-foldable electrodes involves mixing an appropriate amount of CNTs and $LiFePO_4$ particles in a

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Figure 1. Design Scheme of the Super-Foldable Lithium-Ion Battery. Introduces a "three-in-one" biomimetic approach that synchronizes three key processes in one streamlined route: a) silkworm cocoons, b) lotus roots, c) bean-pods. d) Depicts the electrospinning process used to create precursor fiber networks. e) Shows the precursor fiber networks made of LiFePO₄/CNTs@PAN encapsulated in PAN. f) Illustrates the hierarchical structure of a single biomimetic fiber. Demonstrates the creation of super-foldable electrodes through a "one stone, three birds" strategy: g) super-foldable LiFePO₄/CNTs@CFs electrode, h) super-foldable Fe₂P/CNTs@CFs, i) super-foldable substrate. j) A model of the super-foldable battery. Features the super-foldable battery's capability: k) fold for extensive times, l) fold at any angles, m) highlight its infinite flexibility for wearable technology applications.

dimethylformamide (DMF) solution containing PAN, utilizing a "three-in-one" biomimetic strategy for one-step formation. We have carried out multi-step optimization processing in the sample synthesis process. Detailed analysis is available in the supporting information Figures S2–S8 (Supporting Information), and only the optimal sample is discussed in text. By carefully adjusting the co-pyrolysis carbonization temperature, we successfully obtained the super-foldable self-supporting SCLiCF cathode and SCFeCF anode (Figure 2a,d). Scanning electron microscopy (SEM) analysis revealed an interwoven multi-layer network structure with no visible fractures or cross-linkages between fibers, maintaining a consistent fiber width of \approx 675 nm. This design, particularly the encapsulation of LiFePO4 particles within the fibers, prevents active material loss during mechanical bending and charge-discharge cycles. The interconnected fiber network enhances electron transport, while an amorphous carbon layer on the particle surface mitigates volume expansion during Li+ de/intercalation, ensuring structure stability.^[47]

Nitrogen (N₂) adsorption–desorption tests indicated a specific surface area of 102 m² g⁻¹ for the cathode, with a predominant pore size of \approx 2.36 nm (Figure S9, Supporting Information), facilitating stress dispersion during bending and electrolyte infiltration into the fiber membrane. Transmission electron microscopy (TEM) showed that LiFePO₄ particles are uniformly dispersed within the fibers in a "cabin" structure, with CNTs radially arranged, enhancing flexibility and the radial strength akin to the tubular structure in the lotus stems (Figure 2b; Figure

S6, Supporting Information). High-Resolution TEM (HRTEM) (Figure 2c) confirmed the LiFePO₄ particles' crystallinity, aligning with the (311) crystal plane. X-ray diffraction (XRD) characterization (Figure 2g) displayed broad carbon peaks and sharp LiFePO₄ and CNTs diffraction peaks, indicating the amorphous nature of carbon and the high crystallinity of LiFePO₄ particles.

Under the co-pyrolysis at 800 °C, LiFePO₄ decomposes into Fe_2P and Li_3PO_4 phases due to excess carbon reduction, following the reaction:^[48,49]

$$6\text{LiFePO}_4 + 8\text{C} \rightarrow 3\text{Fe}_2\text{P} + 2\text{Li}_3\text{PO}_4 + \text{P} + 8\text{CO}_2 \tag{1}$$

SEM, TEM images, and N_2 adsorption–desorption tests (Figure 2d–f; Figures S10 and S11, Supporting Information) reveal that the anode shares the cathode's mesoporous structure, showcasing no signs of fracturing. HRTEM images (Figure 2f) display a clear lattice spacing of 0.22 nm, aligning with the Fe₂P phase's (111) crystal face, indicating high crystallinity. The shifts in P 2p and Fe 2p peaks observed in XPS analyses (Figures S12 and S13, Supporting Information) further confirm the formation of Fe₂P. A notable absence of significant LiFePO₄ diffraction peaks in the XRD pattern (Figure 2h) suggests a complete transformation, corroborated by Linear Sweep voltammetry (LSV) results at high potentials (Figure S14, Supporting Information). Element mapping illustrates a homogeneous distribution of C, N, O, Fe, and P, (Figure 2i; Figure S10, Supporting Information), emphasizing the uniformity in structural design. Raman

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Figure 2. Morphological and Structural Characterizations of the Biomimetic Electrodes. a) SEM images, b) TEM images (inset: cross-sectional view of the fiber), c) and HRTEM images of the SCLiCF electrode. d) SEM images, e) and TEM images, f) HRTEM images of the SCFeCF electrode. g) XRD patterns of SCLiCF, h) SCFeCF electrodes. i) Elemental mappings of the SCLiCF electrode.

spectroscopy reveals a sharp 2D peak due to the incorporation of CNTs, and a relatively high I_D/I_G ratio (Figure S15, Supporting Information), both vital for the super-foldable battery's performance.

Before assessing the electrode's foldability, preliminary experiments involving intense twisting, rolling, and folding showed the electrodes could revert to their initial state without noticeable damage (Figure S16, Supporting Information). The initial manual folding process, which could take several months and lacked standardization, highlighted the need for an automated folding apparatus for comprehensive and standardized folding tests. Through an in situ auto-dynamic folding test (**Figure 3a**, Figure S17, Supporting Information), the electrodes demonstrated remarkable foldability, with their resistance ratio remaining essentially unchanged after 500 000 true folding cycles (Figure 3b; Video S1, Supporting Information). This confirms the SCLiCF electrode's superior foldability, setting a benchmark for superfoldable battery fabrication.

Further SEM analysis of the SCLiCF electrode in a 180° true folding state revealed strongly folded fiber membranes equipped with a unique foldable device (Figure **S18**, Supporting Infor-

mation), remaining intact without damage. A slight loosening exposes a distinct "M" adaptive structure (Figure 3c), enabling stress to disperse from three directions effectively. This design, along with the biomimetic incorporation of CNTs and active particles, ensures minimal impact on the folding process. Therefore, it can withstand more than 500 000 times of true folding tests without significant fibers breakage at the crease (Figure 3d–f). The electrode's unparalleled foldability is attributed to micro-slidable layers, wave-like smooth fibers, ordered mesopores within the fibers, and an extensive network structure across the fiber membrane, facilitating complete stress dispersion. The super-foldable anode exhibits similar folding performance, with detailed characterizations provided in Figures S19 and S20 (Supporting Information).

Next, we evaluate the electrochemical performance of superfoldable electrodes using various electrochemical techniques. The highly consistent CV curves demonstrate a completely reversible Li⁺ de/intercalation process in the SCLiCF electrode (Figure 3g). Furthermore, the b values are 0.69 and 0.74 for cathodic and anodic peaks (Figure S21a, Supporting Information), respectively, implying that pseudocapacitive behavior is playing



Figure 5. Electrochemical Performance and Durability of the Electrodes. a) Folding process of a sample with the automatic foldable device. b) Changes in resistivity over 500 000 folding cycles. c) SEM images capture the electrode in its folded state. d) SEM images of the SCLiCF electrode at the creases after undergoing 500 000 folding cycles. The enlarge SEM images of two stress dispersion arcs at the creases: e) stress dispersion arcs on the left and f) stress dispersion arcs on the right. g) CV curves, and h) rate performance of the SCLiCF electrode. i) CV curves and j) rate performance of the SCFeCF electrode. k) 3D charge density diagrams for Li⁺ adsorption on different materials: SCF, Fe₂P, SCFeCF. I) Adsorption energy values for different materials concerning Li⁺.

an important effect.^[50,51] The synergy of these processes contributes to the electrode's excellent rate performance (Figure 3h). Specifically, the SCLiCF electrode exhibits specific capacities of 140.6, 126.2, 113.2, and 98.8 mAh g⁻¹ at current rates of 0.15, 0.2, 0.5, and 1C, respectively. When the current density is reversed to 0.5, 0.2, and 0.15C, the capacity recovers to 117.7, 123.3, and 145.7 mAh g⁻¹, respectively, indicating a high-capacity recovery rate of over 98%. Additionally, after 1000 cycles, the electrode maintains a capacity of 110.45 mAh g⁻¹, preserving \approx 98% of its initial capacity (Figure S21b,c, Supporting Information). Overall, the unique 3D conductive network structure of SCLiCF electrodes significantly enhances electron transfer, resulting in satisfactory electrochemical performance. Even after extensive cycling, the SCLiCF electrode retains high crystallinity, flexibility, and dispersed, nonadhesive fibers without any signs of fracture (Figure S22, Supporting Information).

Similarly, the SCFeCF electrodes also exhibit good reversibility in the Li⁺ de/intercalation process, except for the initial activation cycle (Figure 3i).^[50–54] This is consistent with the stability observed in short-cycle tests (Figure S23a,b, Supporting Information). In comparison to the super-foldable carbon nanofiber films (SCF) electrode, the SCFeCF electrode demonstrates superior rate performance, delivering discharge capacities of 517.1, 418.2, 346.2, 281.3, 245.5, and 198.3 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g⁻¹, respectively (Figure 3). The remarkable electrochemical performance of the SCFeCF electrode is attributed to the introduction of Fe₂P and the adsorption contribution from defective carbon. Notably, the SCFeCF electrode showed excellent cyclic stability. Especially at a high current density of 2 A g⁻¹, the battery demonstrates almost no capacity loss after 1000 cycles, showcasing its exceptional cycle stability (Figure S23c, Supporting Information). Electrochemical



impedance (EIS) and detailed charge kinetics analyses were conducted to understand this excellent performance further (Figures S24 and S25, Supporting Information).^[50,51] These analyses revealed that the SCFeCF electrode has a lower charge transfer resistance, faster Li⁺ diffusion rates, and higher pseudocapacitance characteristics (detailed analysis available in the supporting information). The superior electrochemical performance of the SCFeCF electrode is mainly due to increased conductivity, abundant ion transport channels, and more defect sites. Similar to the SCLiCF electrode, the SCFeCF electrode also maintains good flexibility after cycling (Figure S26, Supporting Information).

To explore the impact of Fe_2P particles on the SCFeCF electrode's performance at the electronic and atomic levels, Density Functional Theory (DFT) calculations were performed. These calculations aimed to investigate the Li⁺ adsorption energy and electronic structures of various materials (Figure 3k; Figures S27 and S28, Supporting Information). Figure 3K illustrates the 3D charge adsorption difference for the optimized SCF, Fe_2P , and SCFeCF electrodes upon the adsorption of a Li atom. As observed, the charge difference distribution for the Fe_2P particle and SCFeCF electrode adsorbing a Li atom is significantly more localized than that of the SCF electrode. Specifically, the optimal adsorption energy for the SCFeCF electrode is 0.72 eV, whereas the adsorption energies of Li atoms on the SCF electrode and Fe_2P particle are -1.15 and 0.11 eV, respectively (Figure 3l).

2.3. Mechanical Simulation of Stress Changes During Folding

To gain a more intuitive understanding of how biomimetic structures contribute to superior foldability, we conducted finite element simulations. Drawing on SEM images of the superfoldable battery's key components in various folded states (Figure S29, Supporting Information), we observed the formation of a biomimetic M-like structure at the creases post-folding. Detailed examination revealed three distinct structural transformations (Figure 4a): separated layers (Figure 4b), two smooth arcs (Figure 4c), and micro-grooves within the arcs (Figure 4d). These transformations are likely pivotal to the battery's exceptional foldability. Based on these findings, we abstracted typical structural changes at both material and device levels, encompassing single fiber, fiber network, fiber membrane, and the entire battery structure. Through finite element simulations, we clarified their roles in stress dispersion.

For fibers, we constructed two mechanical models: CNTs@PAN and CNTs/LiFePO₄@PAN (Figure S30, Supporting Information). The finite element color maps revealed that, under identical bending stresses, the CNTs in the CNTs/LiFePO₄@PAN model exhibited a more intense red color, indicating that CNTs with a higher modulus enhanced fiber strength. Furthermore, the interaction force between LiFePO₄ particles and fibers was negligible (Figure S31, Supporting Information), validating the cabin-like structure's design advantages. In the case of 2D fiber networks, we developed two mechanical models: a cross-linked layer (Figure 4e) and a slidable layer (Figure 4i). The cross-linked model showed stress concentration and potential fracture under bending due to restricted fiber movement, as evidenced by pronounced red regions (Figure 4f-h). Conversely, the slidable layer model demonstrated minimal stress across various regions even with increased bending angles, owing to the absence of cross-linking points and the resultant free fiber movement, effectively dispersing stress during folding (Figure 4j–l). For the fiber membrane, we compared a conventional bulk structure against a biomimetic slidable layer structure (Figure S32, Supporting Information). The conventional structure showed significant stress concentration at the bend, likely leading to material fracture. In contrast, the biomimetic structure enabled stress to disperse along the bending arc of each layer, preventing excessive stress concentration and enhancing material foldability. These simulation results illustrate the structural-stress dispersion correlation, affirming our design rationale.

Additionally, we developed two pouch battery models: a conventional structure (Figure 4m) and an integrated biomimetic structure (Figure 4o). The conventional model showed increasing stress concentration at the fold as folding angles increased, indicated by a growing red area in the stress distribution contour map, likely leading to battery fracture at the fold (Figure 4n). However, the integrated biomimetic model with a sliding layer effectively dispersed stress at the fold during folding, minimizing layer interaction forces (Figure 4p), and significantly enhancing battery foldability. This innovative multi-level biomimetic/integration strategy not only aligns with our experimental findings but also offers a blueprint for designing other battery materials.

2.4. Performance Evaluation of Full Battery

Despite the successful creation of the super-foldable cathode (SCLiCF) and anode (SCFeCF), assembling super-foldable full batteries that meet our expectations presents challenges. The first issue encountered is the selection of the collector, which necessitates a conductive material that can endure folding without compromising its structure. To address this, we have developed composite materials containing highly conductive, superfoldable substrates through a "three-in-one" strategy, enabling their use as self-supporting electrodes.

When considering separators, it is crucial to select materials that do not compromise the battery's super-foldability. Traditional materials such as glass fibers, nonwoven fabrics, and wood fiber membranes are unsuitable. Instead, Celgard emerges as a more appropriate choice. Furthermore, for the electrolyte, solid or quasi-solid forms adversely affect super-foldability, making liquid organic electrolytes the preferred option. Polyethylene (PE) has been identified as an optimal material for the outer packaging material, thanks to its suitable properties.

During the battery assembly process, it is not only vital to maintain the inherent super foldability of each component but also to ensure coordinated assembly among them. This involves allowing for free sliding between layers, preventing bubble formation, and avoiding short or open circuits during extensive folding. Additionally, the assembled device should be capable of forming a stress-dispersing structure akin to an "M" shape under extensive folding (Figure S29, Supporting Information), inspired by the structure of mature cocoons. This biomimetic approach has enabled us to create the first instance of an SFLIB capable of enduring 500 000 cycles of true folding without





Figure 4. Finite Element Simulation of Super-Foldability. a) "M" fold structure of a soft package battery, along with its detailed enlargement: b) separate layers, c) dispersed arcs and d) slidable fibers. e) The cross-linked layer of the fiber network, and its corresponding stress distributions under bending f) 30°, g) 90°, h) 120°. i) The slidable layer of the fiber network, and its corresponding stress distributions under bending j) 30°, k) 90°, l) 120°. m) Conventional battery structure and its corresponding stress distributions during the folding process (n). o) Integrated bionic battery structure and its corresponding process (p).

significant electrochemical performance degradation. This battery can consistently power an LED clock, maintaining its brightness throughout the folding process (**Figure 5**a).

The basic electrochemical performance of the SFLIB is initially assessed post pre-activation (Figure 5b). Encouragingly, the SFLIB demonstrates discharge capacities of 267.3, 237.17, 207.3, 176.17, and 129.58 mAh g^{-1} at current densities of 0.1, 0.2, 0.5, 1.0, and 2.0 A g^{-1} , respectively. When the current densities are reverted to 1.0, 0.5, 0.2, and 0.1 A g^{-1} , the capacities recover to 168.5, 196.6, 221.5, and 232.6 mAh g^{-1} , respectively, with a coulombic efficiency (CE) approaching 99% and a capacity recovery rate of 88.9%. The GCD curves at different current densities exhibit a similar trend (Figure S33, Supporting Information), showcasing excellent reversibility.

To assess the electrochemical performance stability of the SFLIB under various deformations, we conducted continuous

GCD tests at various folding angles (Figure 5c,d). After 20 cycles of deformation, the battery capacity demonstrated negligible variation, and the GCD curves remained closely aligned, showcasing the SFLIB's exceptional electrochemical stability across different folding scenarios. Furthermore, a long-term cycling test revealed that the SFLIB could deliver a specific capacity of up to 100 mAh g^{-1} at a current density of 0.5 A g^{-1} after 1000 cycles (Figure S33, Supporting Information). To explore the SFLIB's practical potential, we integrated the battery with small electronic devices. The battery maintained a relatively stable voltage and a consistent resistance value across different folding angles (Figure S34, Supporting Information), suggesting that the battery structure remained intact during the folding process. An inset demonstrates the SFLIB's ability to power an LED clock at various angles, indicating not only excellent mechanical properties but also significant practical electrochemical performance.

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Figure 5. Performance and Durability of a Super-Foldable Lithium-Ion Battery. a) Schematic illustration of the super-foldable battery. b) Rate performance, c) cycling performance under different folding angles and d) corresponding GCD curves. e) Voltage change curves of the battery at different folding angles (inset: battery drives an LED digital clock works during multi-angle dynamic folding). f) Cycling performance of the super-foldable lithium-ion battery following various folding cycles (inset: digital photos showcasing the battery's condition before and after being folded).

For a more rigorous evaluation of electrochemical stability through numerous true folding cycles, we replaced the aluminum-plastic film with a PE encasement. Remarkably, the assembled SFLIB continuously powered an LED digital clock for up to 2870 min over more than 10 000 cycles in situ folding cycles (Figure S35, Video S2, Supporting Information). Importantly, the fully charged battery maintained stable voltage levels and powered the LED digital clock during multi-angle dynamic

folding (Figure 5e; Video S3, Supporting Information). To assess the discharging/charging behavior after continuous folding, we performed an in situ folding GCD test. As shown in Figure 5f, during a rigorous 500 000-cycle in situ true folding test, the SFLIB consistently executed normal discharge and charge operations. The capacity remained stable, and the GCD curves showed a good overlap (Figure S36). Notably, the SFLIB's integrity was preserved after 500 000 in situ folding cycles (Figure S37, Supporting ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

Information). Additionally, SEM images of the electrodes posttesting showed that the fibers remained dispersed and nonadhesive, without visible fractures at the crease (Figure S38, Supporting Information). Overall, these findings demonstrate that the SFLIB, leveraging an integrated biomimetic assembly of super-foldable electrodes, not only withstands up to 500 000 folding cycles but also maintains stable electrochemical performance.

3. Conclusion

For the first time, SFLIB has been developed using a multi-level biomimetic/integration strategy, capable of enduring 500 000 true folding cycles while maintaining stable electrochemical performance. This achievement necessitates not only a highly conductive substrate but also the incorporation of a maximum number of active materials without compromising foldability. Through the implementation of a synchronous multi-level biomimetic coupling strategy, super-foldable self-supporting electrodes with high conductivity, strength, and specific capacity have been prepared, effectively addressing the core challenges associated with super-foldable batteries. The SFLIB, assembled using this biomimetic/integration strategy, not only demonstrates a high degree of overlap in GCD curves at various folding angles but also maintains stable electrochemical performance throughout 500 000 in situ true folding cycles. Furthermore, the reinforcement effect of CNTs within fibers and the multi-level stress dispersion mechanism in electrodes and batteries during the folding process has been systematically analyzed through finite element simulation. Overall, this represents a full-chain innovation process extending from super-foldable substrates to electrodes to super-foldable batteries. This application of multi-level/integrated biomimetic strategies and co-coupling technologies offers a universal guiding principle for designing other super-foldable electronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

biomimetic, foldability, full battery, wearable bioelectronics

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- S. Wang, J. Xu, W. Wang, G.-J. N. Wang, R. Rastak, F. Molina-Lopez, J. W. Chung, S. Niu, V. R. Feig, J. Lopez, T. Lei, S.-K. Kwon, Y. Kim, A. M. Foudeh, A. Ehrlich, A. Gasperini, Y. Yun, B. Murmann, J. B. H. Tok, Z. Bao, *Nature* **2018**, *555*, 83.
- [2] Y. Zhou, X. Zhao, J. Xu, Y. Fang, G. Chen, Y. Song, S. Li, J. Chen, Nat. Mater. 2021, 20, 1670.
- [3] X. Zhao, Y. Zhou, J. Xu, G. Chen, Y. Fang, T. Tat, X. Xiao, Y. Song, S. Li, J. Chen, Nat. Commun. 2021, 12, 6755.
- [4] X. Zhao, Y. Zhou, Y. Song, J. Xu, J. Li, T. Tat, G. Chen, S. Li, J. Chen, Nat. Mater. 2024, 23, 703.
- [5] J. Yin, S. Wang, T. Tat, J. Chen, Nat. Rev. Bioeng. 2024, 2, 541.
- [6] F. Yi, H. Ren, J. Shan, X. Sun, D. Wei, Z. Liu, Chem. Soc. Rev. 2018, 47, 3152.
- [7] Z. Wu, Y. Wang, X. Liu, C. Lv, Y. Li, D. Wei, Z. Liu, Adv. Mater. 2019, 31, 1800716.
- [8] Z. Hui, L. Zhang, G. Ren, G. Sun, H.-D. Yu, W. Huang, Adv. Mater. 2023, 35, 2211202.
- [9] Z.-Y. Chen, D. Yin, J. Feng, Adv. Opt. Mater. 2023, 11, 2300282.
- [10] W. Liu, J. Chen, Z. Chen, K. Liu, G. Zhou, Y. Sun, M. S. Song, Z. Bao, Y. Cui, Adv. Energy Mater. 2017, 7, 1701076.
- [11] X. Xiao, X. Xiao, Y. Zhou, X. Zhao, G. Chen, Z. Liu, Z. Wang, C. Lu, M. Hu, A. Nashalian, S. Shen, K. Xie, W. Yang, Y. Gong, W. Ding, P. Servati, C. Han, S. X. Dou, W. Li, J. Chen, *Sci. Adv.* **2021**, *7*, eabl3742.
- [12] X. Xiao, J. Yin, S. Shen, Z. Che, X. Wan, S. Wang, J. Chen, Curr. Opin. Solid State Mater. Sci. 2022, 26, 101042.
- [13] J. Wan, J. Xie, X. Kong, K. Liu, F. Shi, A. Pei, W. Chen, J. Chen, X. Zhang, L. Zong, J. Wang, J. Qin, Y. Cui, *Nat. Nanotech* **2019**, *14*, 705.
- [14] M. J. Kim, H. S. Ryu, Y. Y. Choi, D. H. Ho, Y. Lee, A. Tripathi, J. H. Son, Y. Lee, S. Kim, M. S. Kang, H. Y. Woo, J. H. Cho, *Sci. Adv.* 2021, 7, eabg8169.
- [15] H. W. Choi, D.-W. Shin, J. Yang, S. Lee, C. Figueiredo, S. Sinopoli, K. Ullrich, P. Jovančić, A. Marrani, R. Momentè, J. Gomes, R. Branquinho, U. Emanuele, H. Lee, S. Y. Bang, S.-M. Jung, S. D. Han, S. Zhan, W. Harden-Chaters, Y.-H. Suh, X.-B. Fan, T. H. Lee, M. Chowdhury, Y. Choi, S. Nicotera, A. Torchia, F. M. Moncunill, V. G. Candel, N. Durães, K. Chang, et al., *Nat. Commun.* **2022**, *13*, 814.
- [16] Y. Mao, G. Li, Y. Guo, Z. Li, C. Liang, X. Peng, Z. Lin, Nat. Commun. 2017, 8, 14628.
- [17] D. Kim, A. Sarkar, J.-H. Ahn, Small 2021, 17, 2006262.
- [18] M. Jian, C. Wang, Q. Wang, H. Wang, K. Xia, Z. Yin, M. Zhang, X. Liang, Y. Zhang, *Sci. China Mater.* **2017**, *60*, 1026.
- [19] Z. Wu, K. Liu, C. Lv, S. Zhong, Q. Wang, T. Liu, X. Liu, Y. Yin, Y. Hu, D. Wei, Z. Liu, Small 2018, 14, 1800414.
- [20] Y. Yan, X. Liu, J. Yan, C. Guan, J. Wang, Energy Environ. Mater. 2021, 4, 502.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [21] Y. Wang, T. Yokota, T. Someya, NPG Asia Mater 2021, 13, 22.
- [22] X. He, Y. Hu, R. Chen, Z. Shen, K. Wu, Z. Cheng, P. Pan, *Chem. Eng. J.* 2019, *360*, 1020.
- [23] R. Huang, M. Huang, X. Li, F. An, N. Koratkar, Z.-Z. Yu, Adv. Mater. 2018, 30, 1707025.
- [24] L. Liu, Z. Niu, L. Zhang, W. Zhou, X. Chen, S. Xie, Adv. Mater. 2014, 26, 4855.
- [25] X. Liu, S. Zou, K. Liu, C. Lv, Z. Wu, Y. Yin, T. Liang, Z. Xie, J. Power Sources 2018, 384, 214.
- [26] D. Wei, W. Shen, T. Xu, K. Li, L. Yang, Y. Zhou, M. Zhong, F. Yang, X. Xu, Y. Wang, M. Zheng, Y. Zhang, Q. Li, Z. Yong, H. Li, Q. Wang, *Mater. Today Energy* **2022**, *23*, 100889.
- [27] W. Shen, K. Li, Y. Lv, T. Xu, D. Wei, Z. Liu, Adv. Energy Mater. 2020, 10, 1904281.
- [28] Y. Yang, S.-W. Ng, D. Chen, J. Chang, D. Wang, J. Shang, Q. Huang, Y. Deng, Z. Zheng, Small 2019, 15, 1902071.
- [29] Q. Cheng, Z. Song, T. Ma, B. B. Smith, R. Tang, H. Yu, H. Jiang, C. K. Chan, Nano Lett. 2013, 13, 4969.
- [30] X. Ge, S. Cao, Z. Lv, Z. Zhu, Y. Tang, H. Xia, H. Zhang, J. Wei, W. Zhang, Y. Zhang, Y. Zeng, X. Chen, Adv. Mater. 2022, 34, 2206797.
- [31] 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.
- [32] B. Wang, J. Ryu, S. Choi, G. Song, D. Hong, C. Hwang, X. Chen, B. Wang, W. Li, H.-K. Song, S. Park, R. S. Ruoff, ACS Nano 2018, 12, 1739.
- [33] X. Yu, X. Zhao, W. Zhao, R. Xu, Y. Liu, H. Shen, Energy Stor. Mater. 2019, 19, 330.
- [34] Q.-C. Liu, L. Li, J.-J. Xu, Z.-W. Chang, D. Xu, Y.-B. Yin, X.-Y. Yang, T. Liu, Y.-S. Jiang, J.-M. Yan, X.-B. Zhang, *Adv. Mater.* 2015, *27*, 8095.
- [35] K. Li, W. Shen, T. Xu, L. Yang, X. Xu, F. Yang, L. Zhang, Y. Wang, Y. Zhou, M. Zhong, D. Wei, *Carbon Ener.* **2021**, *3*, 916.

[36] K. Keum, J. W. Kim, S. Y. Hong, J. G. Son, S.-S. Lee, J. S. Ha, Adv. Mater. 2020, 32, 2002180.

www.afm-journal.de

- [37] Z. Yan, S. Luo, Q. Li, Z.-S. Wu, S. Liu, Adv. Sci. 2023, 11, 2302172.
- [38] Y. Sun, R. B. Sills, X. Hu, Z. W. Seh, X. Xiao, H. Xu, W. Luo, H. Jin, Y. Xin, T. Li, Z. Zhang, J. Zhou, W. Cai, Y. Huang, Y. Cui, *Nano Lett.* **2015**, 15, 3899.
- [39] Z. Wei, T. Liu, L. Zhang, J. Yu, Energy Environ. Mater. 2022, 5, 883.
- [40] J. Li, Y. Shao, Q. Shi, C. Hou, Q. Zhang, Y. Li, R. B. Kaner, H. Wang, Nano Energy 2017, 38, 428.
- [41] Q. Qin, J. Liu, W. Mao, C. Xu, B. Lan, Y. Wang, Y. Zhang, J. Yan, Y. Wu, Nanoscale 2018, 10, 7377.
- [42] D. Ge, L. Yang, L. Fan, C. Zhang, X. Xiao, Y. Gogotsi, S. Yang, Nano Energy 2015, 11, 568.
- [43] K. K. Fu, J. Cheng, T. Li, L. Hu, ACS Energy Lett. 2016, 1, 1065.
- [44] H. Nishide, K. Oyaizu, Science 2008, 319, 737.
- [45] D. G. Mackanic, M. Kao, Z. Bao, Adv. Energy Mater. 2020, 10, 2001424.
- [46] G. Zan, T. Wu, F. Zhu, P. He, Y. Cheng, S. Chai, Y. Wang, X. Huang, W. Zhang, Y. Wan, X. Peng, Q. Wu, *Matter* **2021**, *4*, 3232.
- [47] J. Wang, X. Sun, Energy Environ. Sci. 2012, 5, 5163.
- [48] W. Yang, L. Zhang, Y. Chen, H. Yao, J. Li, Y. Lin, Z. Huang, Appl. Surf. Sci. 2020, 521, 146389.
- [49] Y. Xu, Y. Lu, L. Yan, Z. Yang, R. Yang, J. Power Sources 2006, 160, 570.
- [50] P. Peng, F. Yang, X. Li, S. Li, Z. Wang, D. Wei, Cell Rep. Phys. Sci. 2024, 5, 101824.
- [51] F. Yang, P. Peng, Z.-Y. Yan, H. Fan, X. Li, S. Li, H. Liu, T.-L. Ren, Y. Zhou, Z. L. Wang, D. Wei, *Nat. Energy* **2024**, *9*, 263.
- [52] Z. Wang, K. Dong, D. Wang, F. Chen, S. Luo, Y. Liu, C. He, C. Shi, N. Zhao, *Chem. Eng. J.* **2019**, *371*, 356.
- [53] J. Yang, Y. Ouyang, H. Zhang, H. Xu, Y. Zhang, Y. Wang, J. Mater. Chem. A 2016, 4, 9923.
- [54] Z. Zheng, H.-H. Wu, H. Liu, Q. Zhang, X. He, S. Yu, V. Petrova, J. Feng, R. Kostecki, P. Liu, D.-L. Peng, M. Liu, M.-S. Wang, ACS Nano 2020, 14, 9545.