UTS UNIVERSITY OF TECHNOLOGY SYDNEY

Realizing flexible batteries from material to manufacturing process

by Tao Huang

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Doctor of Philosophy

under the supervision of Hao Liu and Guoxiu Wang

University of Technology Sydney
Faculty of Science

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Certificate of Original Authorship

I, Tao Huang, declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science at the University of Technology Sydney.

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Tao Huang

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Authorship Attribution Statement

The format of this thesis is a "Conventional Thesis".

The published and publishable works included in this thesis, unless otherwise indicated, are all derived from my original research during my doctoral candidature.

- **Chapter 1** of this thesis incorporates sections from the following published works.

Huang, T., Long, M., Xiao, J., Liu, H., & Wang, G. (2021). Recent research on emerging organic electrode materials for energy storage. *Energy Materials*, 1(1):100009. https://doi.org/10.20517/energymater.2021.09

Note. As the first author, I contributed to the outline design, literature collection, figure organization, and manuscript writing of this review.

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- **Chapter 2** of this thesis incorporates the following published work.

Huang, T., Gao, H., Chen, J., Liu, H., Wu, D., & Wang, G. (2022). A book-like organic based electrode with high areal capacity for high performance flexible lithium/sodium-ion batteries. *Chemical Communications*, *58*(73), 10158-10161. https://doi.org/10.1039/D2CC03297J

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- **Chapter 3** of this thesis incorporates the following work.

Huang T., Yang X., Xiao J., Gao H., Liu H., Wang G., Pioneering Uniaxial Fiber Batteries: Structural Innovation for Enhanced Performance in Wearable Electronics. Ready for Submitting.

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As the supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution statements above are correct.

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Abstract

In recent years, the rapid development of portable and wearable electronics has driven a surge in demand for flexible energy storage devices. This PhD thesis presents a comprehensive study of flexible batteries, covering the entire process from material selection to manufacturing processes.

The thesis contributes to the field through literature review and experimental progress. First, this paper presents a comprehensive review of organic electrode materials, exploring their potential applications in flexible batteries due to their inherent flexibility, lightweight properties, and environmental friendliness. This review provides a detailed analysis of various organic compounds, focusing on their electrochemical properties and integration potential with flexible energy storage systems. Another perspective discusses the future prospects of one-dimensional (1D) and two-dimensional (2D) flexible batteries. By evaluating recent advances and emerging trends, the perspective discusses the unique properties of 1D and 2D flexible batteries, such as enhanced mechanical flexibility and high electrical conductivity, which make them suitable candidates for the next generation of flexible energy storage devices. In the experimental section, the thesis research includes the development of book-shaped flexible electrodes, which have been successfully applied to flexible sodium-ion and lithium-ion batteries. These electrodes exhibit excellent mechanical durability and electrochemical properties, demonstrating their practical application potential in flexible energy storage devices. In addition, the thesis designs an innovative uniaxial fiber battery structure specifically for flexible and wearable devices. The novel design enhances the mechanical resilience and energy density of the battery, making it very suitable for integration into a variety of wearable electronic devices.

From material innovation to structural design, the thesis provides insights into the development of flexible batteries, and the research results proposed not only promote the understanding of flexible energy storage systems, but also explore the path for their practical application in the rapidly developing field of wearable technology.

Introduction

With the development of various wearable technologies, people's demand for flexible batteries is increasing. These flexible batteries or flexible capacitors have the unique ability to seamlessly adapt to the wearer's movements, ensuring uninterrupted power supply for a range of smart devices. Studying how to prepare flexible energy storage devices from the aspects of flexible materials and structural innovation has become a very scientific and promising topic.

This paper has made extensive explorations on how to prepare flexible batteries. From material selection to structural innovation, from one-dimensional flexibility to two-dimensional flexibility, by selecting appropriate materials and structures, flexible batteries of different latitudes have been prepared. And each flexible battery finally works and is used in different wearable devices.

The significance of this study is to explore the methods of realizing flexible energy storage devices from different angles and dimensions, and to conduct preliminary exploration of the wearable application of flexible energy storage devices.

The outline of this thesis is as follows.

- **Chapter 1** reviews the research progress of flexible batteries and the application of organic materials in batteries. Organic materials are widely used in flexible batteries due to their advantages such as low cost, non-toxicity, and easy design. The development of flexible batteries involves other research, such as structural innovation, in addition to material research. These material and structural innovations are applied in one-dimensional and two-dimensional flexible batteries, and the stretching, bending, and twisting flexibility of these batteries are summarized.
- **Chapter 2** reports a thick but flexible book-shaped electrode was developed. This electrode can be combined into dozens of layers, and the current can be collected and exported or imported through the spine. At the same time, each layer of the electrode has a porous structure, which will not affect the flow of ions from the

innermost layer to the outermost layer. The entire book-shaped electrode can maintain good electrical conductivity and ion conduction capabilities in the state of dozens of layers, and the specific area capacity increases multiplied with the number of layers. At the same time, the bending flexibility of this electrode has also been systematically studied. Finally, this electrode was successfully used in flexible lithium-ion batteries, and then this flexible battery was used in smart Android watches, smart insoles, and flexible LED arrays.

- **Chapter 3** presents a new type of uniaxial fiber battery. Compared with traditional multi-axis fiber batteries, the cathode and anode of uniaxial fiber batteries always maintain a fixed distance, which makes this fiber battery inherit the advantages of flat battery, and the rate discharge performance is much higher than that of traditional multi-axis fiber batteries. At the same time, the cathode and anode of the uniaxial fiber battery always remain face to face, so that all cathode and anode areas remain electrochemically active, and there will be no inactive areas of traditional multi-axis fiber batteries. While having these electrochemical performance advantages similar to those of flat batteries, the uniaxial fiber battery also maintains the appearance of a fiber battery, allowing it to be woven into cloth for a wide range of wearable applications.
- **Chapter 4** This chapter summarizes the entire thesis work. At the same time, it provides a reasonable summary and outlook on the development prospects and research directions of flexible batteries and flexible energy storage devices. This paper hopes to arouse more people's interest and attention in flexible energy storage devices, and promote the research progress and practical application of this research direction.

Chapter 1: Literature Review

1.1 OVERVIEW OF ORGANIC ELECTRODE MATERIALS

With more attention to green energy by society, wind power (Jafarzadeh Ghoushchi et al., 2021), photovoltaic power (J. Li et al., 2021), tidal power (Ghaedi & Gorginpour, 2021) generation are gradually squeezing out of traditional power generation. These power generation systems are unstable, and the power supply and user demand are inconsistent. Thus, power generation systems must be equipped with secondary batteries to store excess electricity (Dicorato et al., 2012), leading to increased demand for energy storage batteries. There is also growing demand for energy storage batteries in other markets, such as smart electronic devices and new energy vehicles. These smart devices use lithium-ion batteries and polymer lithium-ion batteries, while Uninterrupted Power System and vehicle start-up systems commonly use lead-acid batteries (Wang & Zhu, 2020).

Early batteries were composed of metals with different electrochemically active potentials, such as the famous Voltaic Pile. Later, the battery developed into a rechargeable type. The electrode materials consist of metal oxides, metal salts, metals, etc. (Browne et al., 2019; Joshi et al., 2014; Liao et al., 2016; Shukla et al., 2015), have been applied in rechargeable batteries such as the lead-acid battery (PbO2-Pb), nickel-cadmium battery [NiO(OH)-Cd], lithium-ion battery (LiCoO2-C, LiFePO4-C, etc.). Most of the electrode materials of these batteries belong to inorganic materials, exhibiting high price, heavy metal toxicity, environmental pollution, and degradable recycling, which need further attention for energy storage applications (Bashir et al., 2019; Qiu et al., 2021). Now, lithium-ion batteries and lead-acid batteries currently have the highest market share (Weinert et al., 2007; Zou et al., 2018), and lead-acid batteries have achieved a closed loop of production-using-recycling-reproduction. In contrast, lithium-ion batteries have not yet formed an effective market-oriented recycling and reuse program, which leads to serious waste and pollution of electrode materials. Moreover, the resource of cobalt and lithium elements for the fabrication of lithium-ion batteries is unevenly distributed around the world, leading to the unstable cost of electrode materials (Huang et al., 2018; Ryu et al., 2021).

With the increasing demand for lithium-ion batteries in electric vehicles, subsequent production requires a large amount of lithium (Huang et al., 2018), cobalt, nickel, manganese, and other elements. At the same time, after the service life of a large number of lithium-ion batteries in electric vehicles expires, there is no effective recycling procedure, and the batteries are directly discarded, causing serious pollution and waste of electrode materials. Therefore, it is crucial to look for novel, low-cost, non-toxic, biodegradable electrode materials that can be designed to meet our needs for next-generation batteries.

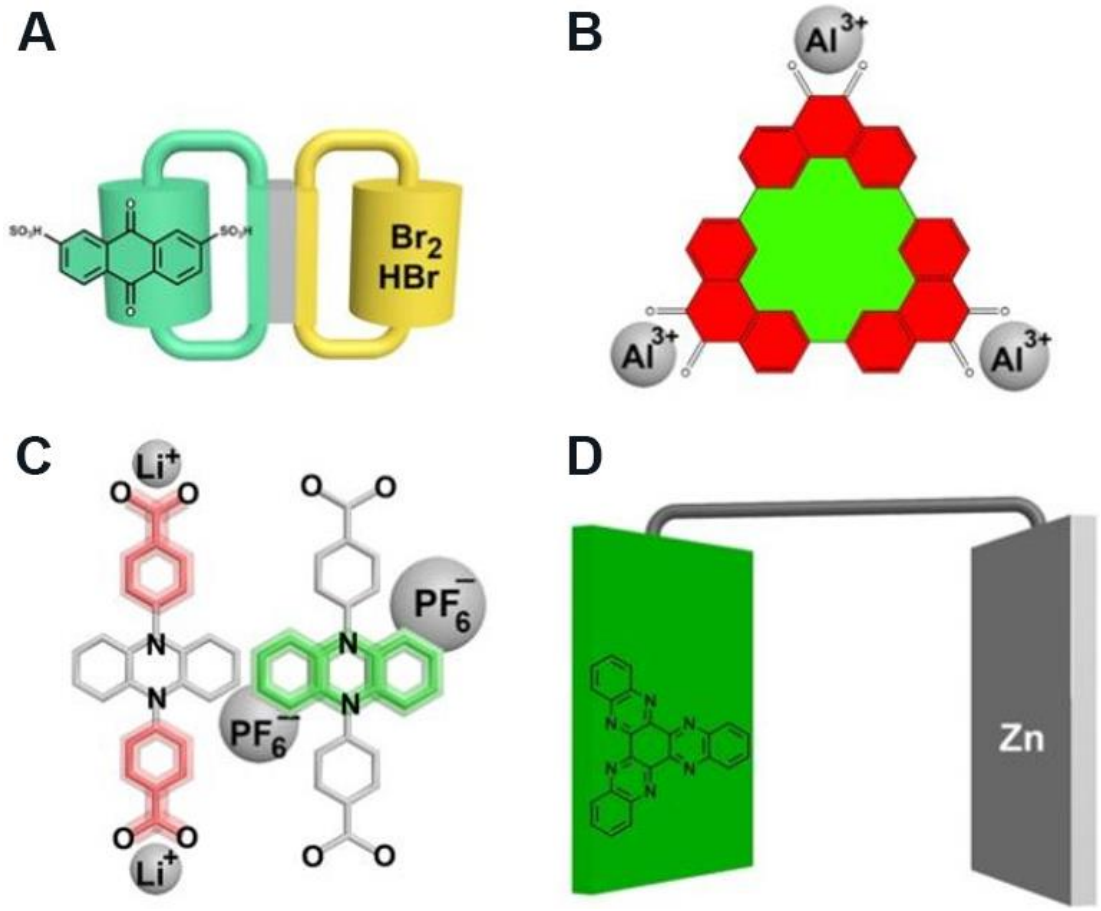
Organic electrode materials have changed this situation (Dantas et al., 2024; Guo et al., 2024; Schon et al., 2016). Organic materials also have oxidation and reduction electrochemical activity and can be used as anode and cathode materials for rechargeable batteries. These materials can be derived from biomass, petroleum industry by-products, etc., regardless of geographical restrictions. The cost of organic electrode materials is affected by the production process. Under the condition of mature and mass production processes, the cost becomes very low. At the end of the battery life, the organic electrode material can be automatically degraded or manually processed into non-toxic and pollution-free substances. At the same time, organic materials can be used in different battery systems by adjusting the length of the carbon chain, functional groups, and other structures. The advantages of emerging organic electrode materials and their applications are summarized as follows.

1.1.1 Low cost

The low cost of organic electrode materials allows them to be used in various types of battery systems. Typically, Quinone materials have been successfully used in flow batteries (Huskinson et al., 2014). The electrode material was 9, 10-anthraquinone-2, 7-disulphonic acid [Figure 1.1 A], which has a rapid and reversible redox reaction and showed a 0.6 W cm^{-2} at 1.3 A cm^{-2} power density.

Figure 1.1

Structure formula of some low-cost organic electrode materials.



Note. (A) 9, 10-anthraquinone-2, 7-disulphonic acid for flow battery. (B) A redox-active triangular phenanthrenequinone-based macrocycle. (C) 4, 4 -(phenazine-5,10-diyl) dibenzoate. (D) The phenazine material for Zn-organic battery.

Organic cathode materials, along with low-cost anode materials (aluminium, zinc, etc. (Wang et al., 2017)), can further reduce battery costs. In 2018, Kim et al. (Kim et al., 2019) applied a redox-active triangular phenanthrenequinone-based macrocycle [Figure 1.1 B] as cathode material into an aluminum battery. The large triangular structure of the material can allow the reversible embedding and detachment of aluminum ions in the redox reaction. This material has very good electrochemical properties, displaying a high revisable capacity of 110 mAh g^{-1}, and a long lifespan of up to 5000 cycles. The electrochemical performances of another two phenanthrenequinone-based materials with a monomer and linear trimer structure have also been studied. The triangular macrocycle structure showed the best result because of its layered architecture and the minimization of solvent effects.

In a symmetrical battery system, the low cost of organic electrode materials will be more obvious because the anode and cathode are the same. Dai et al. (Dai et al., 2019) investigated a dual-ion organic symmetric battery system, which used a molecular anion of 4, 4-(phenazine-5, 10-diyl) dibenzoate [Figure 1.1 C]. For taking advantage of the phenazine and benzoate moieties parts and their electrochemically reversible redox reactions, an artificial bipolar molecular anion was designed and synthesized. The molecular anion had a high average discharge voltage of 2.5 V and an energy density of 127 Wh kg^{-1} at 1 C discharge current.

Zinc-organic battery system is another hot area of organic electrode materials. Tie et al. (Tie et al., 2020) studied a phenazine material [Figure 1D] in the aqueous Zn-organic battery system and got an initial discharge capacity of 405 mAh g^{-1} at 100 mA g^{-1}. The capacity retention was 93.3% after 5000 cycles at 5 A g^{-1}.

Costs of an organic cathode material (p-chloranil) and two common inorganic materials were calculated Table 1. P-chloranil is a mature organic material that represents the cost of organic electrode materials when they are mass-produced. P-chloranil has been successfully used to the cathode in aqueous batteries by Yue et al. (Yue et al., 2021). In his work, the battery uses a p-chloranil material as a cathode and lead as an anode. The p-chloranil has a specific capacity of 200 mAh g^{-1}, and the battery discharge voltage platform is around 1 V. Considering the unit price of p-chloranil is 10 CNY (Chinese Yuan) kg^{-1} (Guidechem, 2021), its watt-hour cost is:

$$\frac{10\ \text{CNY kg}^{-1}}{200\ \text{Ah kg}^{-1}\times 1\text{V}}=0.05\ \text{CNY Wh}^{-1}$$

In the PO_2-Pb lead-acid battery system, the specific capacity of positive electrode material (PbO2) is about 100 mAh g^{-1}, and the battery discharge voltage platform is about 2 V. 207.2 kg Pb raw material corresponds to 239.2 kg PbO_2, and the unit price of the lead ingot is 13 CNY kg^{-1} (Mymetal.net, 2021). The unit price of PbO2 (based on raw lead ingots) per watt-hour is:

$$\frac{13.7\text{CNY kg}^{-1}\times\frac{207.2}{239.2}}{100\ \text{Ah kg}^{-1}\times 2\ \text{V}}=0.06\ \text{CNY Wh}^{-1}$$

In the $LiCoO_2$-graphite lithium-ion battery system, the practical, specific capacity of $LiCoO_2$ is about 140 Ah kg^{-1}, and the battery discharge voltage platform is

about 3.8 V. The unit price of $LiCoO_2$ is about 110 CNY kg^{-1} (1688.com, 2021). Thus, the cost per watt-hour of lithium cobaltate (LCO) in a battery system is:

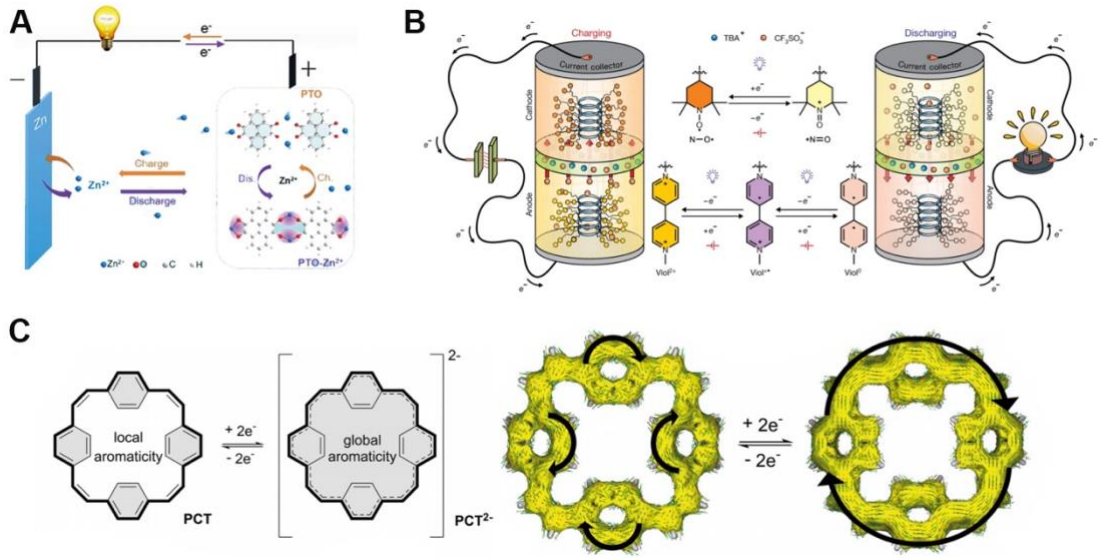
$$\frac{110\ \text{CNY kg}^{-1}}{130\ \text{Ah kg}^{-1} \times 3.8\ \text{V}} = 0.22\ \text{CNY Wh}^{-1}$$

1.1.2 Safe and green

Organic materials can be designed to be non-toxic and environmentally friendly, which gives them advantages in terms of safety and greenery. As an anode material, zinc is also non-toxic and environmentally benign. Therefore, in addition to the low cost, the organic-zinc battery system is also safe and green, which is very suitable for application in wearable electronic devices. Guo et al. (Guo et al., 2018) studied a pyrene-4, 5, 9, 10-tetraone [Figure 1.2A] cathode and zinc anode battery system in a mild aqueous electrolyte. The organic cathode material exhibited a capacity of 336 mAh g^{-1} and an energy density of 186.7 Wh kg^{-1}, and over 1000 cycles of life.

Figure 1.2

Structural formula of some environment-friendly organic electrode materials.



Note. (A) Pyrene-4, 5, 9, 10-tetraone (Guo et al., 2018). (B) Polypeptide anode and cathode polypeptide materials (Tan P. Nguyen et al., 2021). (C) [2.2.2.2]paracyclophane-1, 9, 17, 25-tetraene (Eder et al., 2020).

Biodegradability is another green advantage of organic electrode materials. Because organic materials can be designed into a polypeptide polymer structure, this structure can spontaneously degrade in nature, avoiding the environmental pollution problem. Nguyen et al. (Tan P. Nguyen et al., 2021) synthesized polypeptide materials [Figure 1.2 B] and designed a metal-free organic radical battery, which showed a capacity of 37.8 mAh g^{-1}. They also studied the degradation and toxicity of the materials, and found the cathode polypeptide was deemed non-toxic towards preosteoblast cells, mouse fibroblast cells, and bovine coronary venular endothelial cells, and could be degraded into small molecules.

Aromatic organic materials contain only carbon and hydrogen elements, without oxygen, nitrogen, sulfur, and other elements. Compared with heavy metals and nitrogenous organic matter, they are less toxic, and some of them are even non-toxic. If the materials are used in batteries, it will be very environmentally friendly. Traditional graphite anode materials also contain only carbon but are currently used only in lithium-ion batteries. The large size of sodium and potassium ions limits the use of graphite in the anode electrode of such batteries, while aromatic organic materials solve this problem. Eder et al. (Eder et al., 2020) assessed the possibility of [2.2.2.2]paracyclophane^{-1}, 9, 17, 25-tetraene [Figure 1.2 C] in sodium-ion batteries, which showed a good potential value.

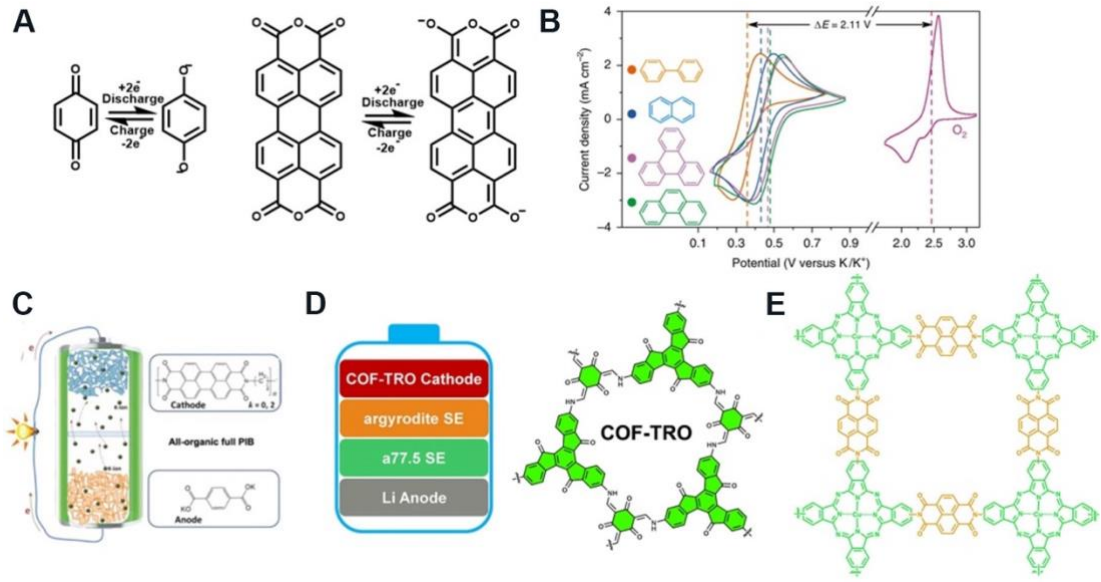
1.1.3 Designable structure

Organic molecules have strong design flexibility by adding and subtracting carbon chains and changing functional groups. These structural changes can alter the electrochemical properties of materials and expand the application fields. In particular, organic electrode materials consist of carbonyl and π conjugate structures. The carbonyl group is the site of the REDOX reaction, and the π conjugate structure provides high conductivity and overall material stability. For example, when p-benzoquinone and 3, 4, 9, 10-perylenetetracarboxylic dianhydride were used as cathode materials, their electrochemical reaction mechanisms are shown in Figure 1.3A. The mechanism of functional group REDOX of organic materials is different from the interlayer embedding and exhalation mechanism of layered inorganic materials. For example, in sodium-ion batteries and potassium-ion batteries, because the ionic radius of sodium-ion and potassium-ion is much larger than that of lithium-ion, the traditional lithium-ion battery electrode materials cannot be directly applied

to sodium-ion batteries and potassium-ion batteries. Organic electrode materials can be directly applied to lithium-ion batteries, sodium-ion batteries, and potassium-ion batteries with the same storage mechanism. Cong et al. (Cong et al., 2019) investigated the redox performance of four aromatic hydrocarbons, including biphenyl, naphthalene, triphenylene, and phenanthrene [Figure 3B]. The redox potentials of these anode materials were 0.35, 0.42, 0.45, and 0.46 V vs. K/K^+, respectively. It's found that the potassium biphenyl showed the best electrochemical performance as an anode in K-O_2 batteries. By adding the electron-donating methyl group to the benzene ring, the biphenyl redox potential can be reduced from 0.35 V to 0.29 V vs. K/K^+.

Figure 1.3

Structural formula and REDOX mechanism of some designable organic electrode materials.



Note. (A) REDOX mechanism of p-benzoquinone and 3, 4, 9, 10-perylenetetracarboxylic dianhydride. (B) From top to bottom are biphenyl, naphthalene, triphenylene, and phenanthrene (Cong et al., 2019). (C) Polymerized PTCDA monomers with different short alkyl chains (Tong et al., 2020). (D) The truxenone-based covalent organic framework material (X. Yang et al., 2020). (E) The conjugated microporous polymers material (H.-g. Wang et al., 2021).

3, 4, 9, 10-perylene-tetracarboxylic acid-dianhydride (PTCDA) is another organic cathode material used in lithium, sodium, and potassium ion batteries. Tong et

al. (Tong et al., 2020) polymerized PTCDA monomers with different short alkyl chains [Figure 1.3C] and studied their electrochemical properties and redox kinetic differences in potassium-organic batteries. They achieved an energy density of 113 Wh kg^{-1}, power of 35.2 kW kg^{-1}, and excellent performance at an ultrahigh discharge current density up to 147 C. The battery capacity loss was near 0 after 1000 cycles at a current density of 7.35 C.

Covalent organic framework materials have a tunable chemical structures, which they can be used in different batteries for various purposes. Yang et al. (X. Yang et al., 2020) reported a truxenone-based covalent organic framework (COF-TRO) material [Figure 1.3D] in all-solid-state lithium-ion batteries as the cathode. The material showed a capacity of 268 mAh g^{-1}, and 99.9% capacity retention after 100 cycles at a 0.1 C rate. The electrode material was synthesized from TRO and 1, 3, 5-triformylphloroglucinol by polymerization under vacuum heating.

Conjugated microporous polymers (CMPs) materials also have redox-active properties and can be tunable. Wang et al. (H.-g. Wang et al., 2021) synthesized and studied the CMPs by integrating copper (II) tetraaminephthalocyanine (CuTAPc) and 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride (NTCDA) units into the RCMPs (CuPcNA-CMP, Figure 3E). They obtained a capacity of 245.3 mAh g^{-1} at the current density of 0.1 A g^{-1}, and 89% capacity retention after 500 cycles. The rate performance was also outstanding, achieving 125.1 mAh g^{-1} at 5 A g^{-1}. And this electrode material was prepared by the dissolution of CuTAPc and NTCDA into DMAc, and then condensation polymerization under vacuum heating. Similar to covalent organic frame materials, CMPs are also organic polymer materials. Their specific capacities are very similar. The theoretical and practical capacities of the same kind of organic electrode materials depend on the number of REDOX functional groups and the molecular weight of the molecule. Therefore, a higher number of electrochemically active functional groups and lower relative molecular weight usually predict higher specific mass capacity.

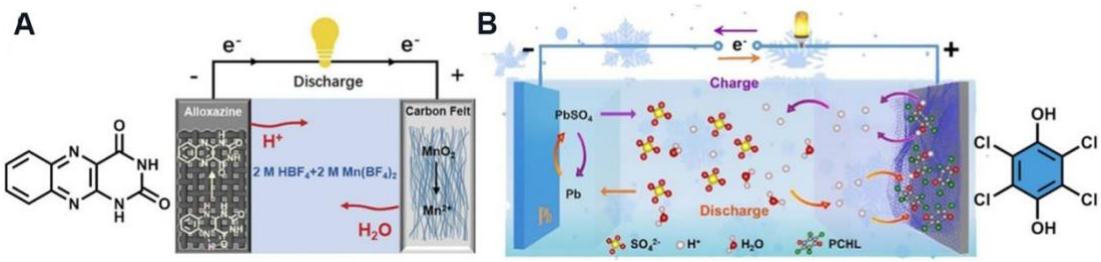
1.1.4 Cryogenic superiority

Organic electrode materials have been widely used in cryogenic batteries because of their easy bonding and detachment to protons. Organic materials that have REDOX activity by binding and releasing protons become a good choice for low

temperature battery electrode materials. Based on this principle, Tie et al.(Tie & Niu, 2020) successfully prepared enhanced zinc-organic batteries with diquinoxalino [2,3-a:2',3'-c] phenazine (HATN) as an electrode material. Tie et al. (Tie & Niu, 2020) also summarized the design strategy of a high-performance aqueous Zn/organic battery. Because aqueous solutions containing acids have a much lower freezing point, and the apparent movement rate of protons in water is very fast, the proton aqueous solution becomes one of the best low temperature electrolytes. Sun et al. (T. Sun et al., 2021) studied alloxazine [Figure 1.4A] material as the anode in aqueous proton battery. This battery delivered a high specific energy density of 110 Wh kg^{-1} at a power density of 1650 W kg^{-1} at -60 °C. When the temperature is lower to an extremely low temperature (-90 °C), the material could also exhibit a discharge capacity of 85 mAh g^{-1}.

Figure 1.4

Structural formula of organic electrode materials in cryogenic batteries.



Note. (A) Alloxazine (T. Sun et al., 2021). (B) P-chloranil (Yue et al., 2021).

Another cathode material, p-chloranil, was successfully applied in an ultralow temperature aqueous battery system. Yue et al. (Yue et al., 2021) reported the p-chloranil [Figure 1.4B] organic material composite with reduced graphene oxide (PCHL-rGO) used in aqueous Pb-quinone batteries. The Pb/PCHL-rGO batteries exhibited a discharge capacity of 87 mAh g^{-1} at a current of 0.1 A g^{-1}. And the cycle retention was 97% after 500 cycles at 0.5 A g^{-1} under -70 °C. This battery system not only has good electrochemical performance at low temperatures, but also is very inexpensive for practical application.

1.1.5 Conclusion and outlook

Compared with traditional inorganic electrode materials, organic electrode materials have many advantages in cost, safety, environmental friendliness, design

diversity, and low temperature battery applications. On the other hand, organic electrode materials also have disadvantages, mainly in poor conductivity, solubility, and low voltage platform. Researchers are constantly working to overcome these shortcomings.

Not all organic electrode materials conduct electricity well, so many organic electrode materials must be mixed with a large number of conductive carbon materials when used in batteries, which affects the overall volume energy density and mass energy density of the battery. Therefore, it is crucial to enhance the intrinsic electronic conductivity of organic materials so that the electrochemical properties can be boosted. Conjugate π structures combined with various functional groups may be an important direction in the future because of their excellent electrical conductivity.

Furthermore, solubility in the electrolyte is another serious problem for organic electrode materials, especially smaller organic monomers. In lithium-ion, sodium-ion, and potassium-ion batteries, organic materials such as small molecules tend to dissolve in the organic electrolyte during charge-discharge cycles. Combining organic materials with a small amount of highly conductive material (such as graphene (Huang et al., 2018), carbon nanotubes, MXene, etc.) seems to be an effective way to solve the problem of poor electronic conductivity as well as the solubility of the electrode active materials. Polymerization of organic monomers into polymers can also solve the problem of material dissolution, but the method of polymerization needs to be explored by researchers. At present, many polymerization methods use organic solvents, some of which are often expensive or harmful to organisms. Finding a method using water polymerization or solvent-free polymerization has become an effective solution.

Compared with cathode materials such as $LiCoO_2$ and ternary materials, organic cathode materials have a lower voltage platform. Lithium-ion batteries made of $LiCoO_2$ have an open circuit potential above 4 V, while the voltage of most organic lithium-ion batteries is between 2 V and 3 V. Due to the decrease of the voltage platform, the energy density of the battery decreases, which affects the cost advantage of the application of organic materials in the battery. This requires researchers to develop novel REDOX groups and combine them with organic host structures.

Although there are still many challenges in developing high-performance organic electrode materials, it is no doubt that the electrochemically active organic electrode materials will attract more attention in the future. With the increasing

demand for rechargeable batteries, the abandonment of traditional battery materials and environmental pollution problems, and the further reduction of the cost of organic materials, the large-scale application of organic electrode materials in various commercial batteries is promising.

In addition, many flexible batteries use flexible base materials that have good compatibility with organic electrode materials. This makes organic electrode materials have a very large natural advantage in flexible batteries.

1.2 OVERVIEW OF ADVANCING LOW-DIMENSIONAL FLEXIBLE ENERGY DEVICES FOR WEARABLE TECHNOLOGY

Flexible batteries and supercapacitors have witnessed remarkable progress in recent years, making them integral to the field of wearable technology. These energy devices offer the unique ability to seamlessly conform to the wearer's movements, ensuring uninterrupted power supply for an array of smart devices. To meet the pressing demand for high-efficiency wearable batteries, it is crucial to explore various forms of flexibility and their impact on practical applications. This perspective critically examines the recent advancements in one-dimensional and two-dimensional flexible energy devices, emphasizing their pivotal roles in enabling wearable technology to reach their full potential. Lastly, the challenges and opportunities associated with these devices are discussed in detail, underscoring the paramount importance of low-dimensional flexible energy solutions in the ever-evolving landscape of wearable devices.

1.2.1 Background

Energy storage devices are indispensable components, and their design must cater to specific physical and chemical properties (Aubin et al., 2019; Chu, 2021; He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, & Zhang, 2021; Kidambi et al., 2021; Kleiner, 2006; Liao et al., 2022; Tan P Nguyen et al., 2021; Zhang et al., 2023) to meet diverse applications scenarios (Held et al., 2018; Ioakimidis et al., 2019; Jiang et al., 2020; Lopes & Stamenkovic, 2020; Sun et al., 2017; Zhao et al., 2020). Traditional power plants, like emerging wind power and solar power stations, demand energy storage devices with large capacity and cost-effectiveness (Chen et al., 2024; Chi et al., 2021; Gao et al., 2024; Janoschka et al., 2015; Hao Liu et al., 2017; X.-M. Lu et al., 2024; Peng et al., 2012; W. Sun et al., 2021), while volume and weight are less

critical (Burheim, 2017; Guo et al., 2022; Z. Li et al., 2021). In contrast, portable electronic devices, such as smartphones and smartwatches, require high energy densities and compact volume, often at the expense of cost considerations (Kang & Ceder, 2009; M. Wang et al., 2021; Xia et al., 2018; Xiao et al., 2021). Electric vehicles occupy an intermediate position, considering a delicate balance between endurance mileage, limited physical dimensions, and the necessity for extra-large capacity, high-energy Density, and cost-effectiveness (Eaves & Eaves, 2004; Gerssen-Gondelach & Faaij, 2012; Lan et al., 2020; Nykvist & Nilsson, 2015; Ovshinsky et al., 1993; Parker et al., 2017; X. Zhou et al., 2020). The emergence of wearable technology has introduced a novel requirement for battery devices – flexibility (Lan et al., 2020; Manjakkal et al., 2021; C. Wang et al., 2020; Wu et al., 2019). These devices need to be capable of bending, twisting and stretching to accommodate the dynamic nature of wearable applications (Chen et al., 2021; X. Chen et al., 2019; Ma et al., 2020; Mackanic et al., 2020; Wang et al., 2018; Wang et al., 2016; Zhang et al., 2016). This necessitates the development of low-dimensional structured flexible batteries and supercapacitors, tailored to varying timelines, battery dimensions, and device types (Figure 1.6). Different wearable scenarios require different types of flexibility. For instance, when integrating flexible battery into soft robots, such as worm robots, stretchable batteries/supercapacitors are vital to accommodate the robots' deformations (Y. Lee et al., 2020; Y. Li et al., 2021; Lu & Kim, 2014). In the case of a watch band (Figure 1.6c), a great degree of bendability to conform to the wrist's shape while optimizing capacity and standby time (Chang et al., 2021; Chen et al., 2021; J. Chen et al., 2019; Xiao et al., 2014; Zhu et al., 2020). In addition, flexible energy devices can be designed into one-dimensional (1-D) rubber band (Man et al., 2019; Song et al., 2019; Wang et al., 2016) or two-dimensional (2-D) films (Figure 2a) (Guo et al., 2017; Jabbour et al., 2010; Wang et al., 2008; Xiong et al., 2015), both capable of stretching, bending and twisting (Figure 1.6.6a and 1.6b).

Figure 1.5

Timeline of the development of typical flexible batteries/supercapacitors. Panels reproduced with permission from Copyright (Wiley), (Elsevier), (Springer Nature), (Royal Society of Chemistry).

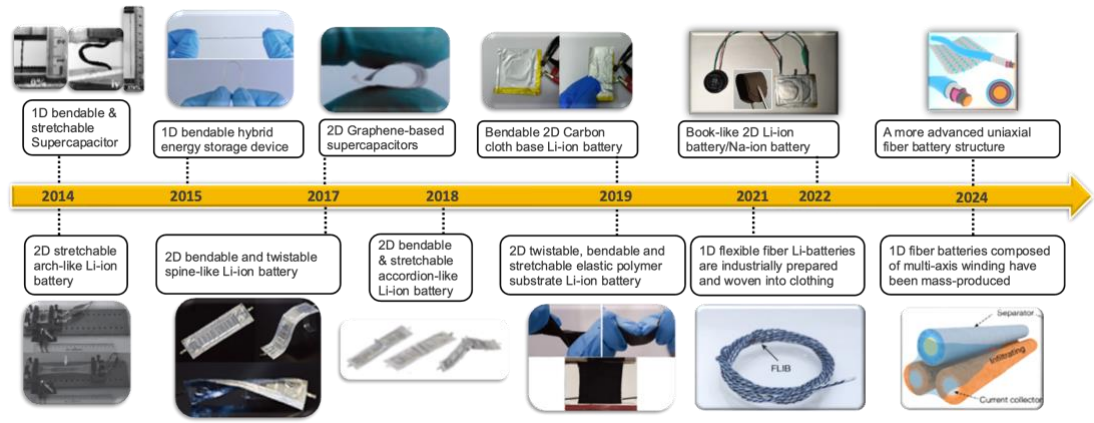
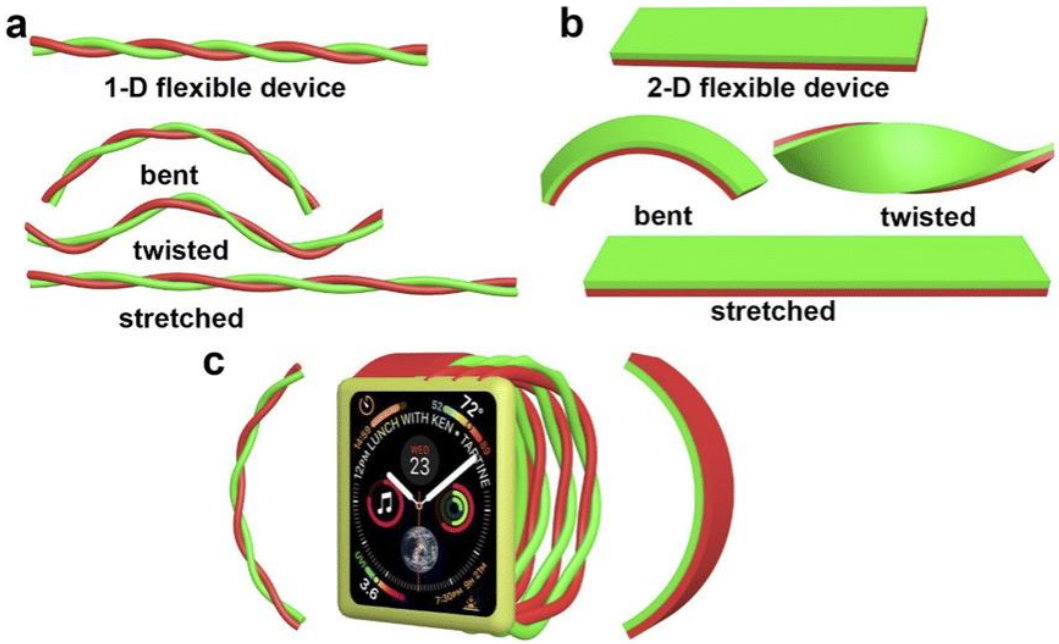


Figure 1.6

Schematic diagram of supercapacitor and battery with different dimensions and flexibility.



Note. (a) A one-dimensional flexible energy storage device and corresponding three flexible states. (b) A two-dimensional flexible energy storage device and corresponding three flexible states. (c) A hypothetical one-dimensional or two-dimensional flexible energy device for smart watches.

These energy devices feature similar components to traditional energy storage systems. They consist of two electrodes, cathode and anode (Asadi et al., 2018; Cao & Zheng, 2013; Srimuk et al., 2016), sometimes with multiple cathodes and anodes connected in series or parallel inside the battery (Boddula et al., 2020). They serve as

the source of energy storage(Liu et al., 2021). In addition, a diaphragm or separator is crucial for separating electrodes and preventing internal short circuit (C. s. Yang et al., 2020). The electrolyte within cell allows electrical current to flow between anode and cathode (Kim & Kim, 1999). All the above substances are encapsulated in a case to insulate them from the outside environment. Flexible energy devices incorporate the same components, albeit in flexible state. To be specific, the flexible energy device is realized from bendable electrode (He et al., 2017; Huang et al., 2016; Tan et al., 2017; D.-W. Wang et al., 2009; Wu & Yao, 2017), elastic electrolyte/diaphragm (Y. J. Kang et al., 2016; Kim et al., 2015; Lei et al., 2018; Li et al., 2018; Moon et al., 2015), as well as pliable packaging material (Jansen et al., 2002; Thomas & Qidwai, 2005). Like the traditional energy storage systems, this type of flexible batteries/supercapacitors also can be applied to super capacitors, lithium-ion batteries, sodium-ion batteries, zinc-ion batteries (Ates et al., 2021; Dong et al., 2018; Liu et al., 2020; Ma & Li, 2021; Shaikh et al., 2021; Uke et al., 2021; Yu et al., 2018), etc.

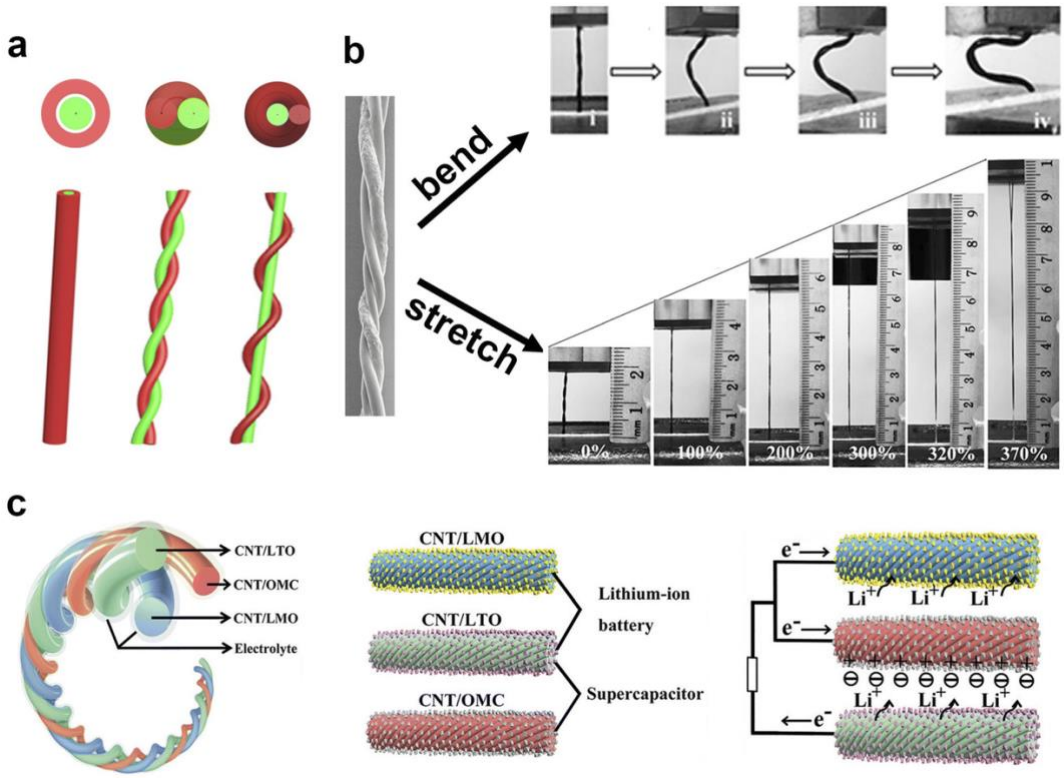
1.2.2 1-D flexible energy devices

A 1-D flexible energy storage string has emerged as a transformative technology. They can be wound around devices or seamlessly woven into clothing, providing a means to store and deliver electrical energy for various electronic applications. This innovation empowers individuals to power electronic devices while wearing smart clothes, ushering in a new era of wearable technology (Lee et al., 2013). Like their traditional batteries' counterparts, 1-D flexible energy devices consist of electrodes, electrolyte, separator and packaging materials, among which electrode research is the main research object. Notably, Peng's group has made a lot of contributions to the research of 1-D flexible batteries/supercapacitors (Chen et al., 2015; Deng et al., 2015; Liao et al., 2022; Ren, Bai, et al., 2013; Wang et al., 2016; Weng et al., 2015; Yang et al., 2013; Yu et al., 2017; Zhang et al., 2016). They explored the fabrication of various 1-D flexible devices, including symmetric supercapacitors, asymmetric supercapacitors and lithium-ion batteries. These devices are further woven into wearable flexible batteries/supercapacitors (He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, & Zhang, 2021; Liao et al., 2022). The remarkable progress made by Peng's research group has resulted in practical fiber batteries, several meters or even tens of meters in length. These extended fibers can be woven into fabrics, and they continue to function reliably after undergoing washing and enduring substantial pressing, and

more importantly, these fiber batteries did not show any safety issues such as smoke, fire or explosion after these treatments (He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, & Zhang, 2021; Liao et al., 2022).

Figure 1.7

Various types of one-dimensional electrodes.



Note. (a) Schematic diagram of three different types of one-dimensional electrodes assembled into a one-dimensional device. (b) Bending and stretching photos of one-dimensional flexible batteries/supercapacitors, in which the distortion of flexible devices can be attributed to bending. (c) A hybrid flexible energy storage device composed of three different types of electrodes, two of which can be composed of a supercapacitor and two of which can be composed of a lithium-ion battery, in which high power density and high energy density can be achieved through different internal and external connections. Panels reproduced with permission from (b) (Chen et al., 2015) (Wiley) and (c) (Zhang et al., 2015) (Wiley).

Generally, the one-dimensional electrode comes in two primary forms. One is coaxial mode (Yu et al., 2017), in which an electrode is used as the axis, then gel electrolyte wraps on it, followed by a layer of coaxial tubular electrode further wraps

on the outer layer as the opposite electrode. The outermost layer is the packaging material to form a coaxial one-dimensional flexible energy device. In the other mode, the two electrodes are wound together (Ren, Bai, et al., 2013), in which the axes spiral each other. In this case, multiple electrodes can be wound to form a flexible 1-D hybrid energy device. Alternatively, one electrode remains stationary while the other electrode winds around it as the counter electrode (Deng et al., 2015; Yang et al., 2013). In this case, the axis of the non-rotating electrode is a straight line, while the counter electrode of axis forms a helix. The schematic representations of these three electrode combinations are depicted in Figure 1.7a. All of these different combinations perform excellent flexibility, enabling them to be stretched, bent or twisted (Figure 1.7b). These advancements in 1-D flexible energy devices are shaping the future of wearable technology and energy storage.

1.2.2.1 Stretchable property of one-dimensional flexible batteries/supercapacitors

1-D energy devices are naturally inclined to bending and distortion, while achieving stretchability poses a significant challenge. In the case of 1-D electrode, resilience is an essential character. Dai's group (Chen et al., 2015) reported a stretchable 1-D flexible capacitor. The flexible capacitor consists of two identical electrodes, forming a symmetric supercapacitor, and the electrolyte/diaphragm is composed of polyvinyl alcohol and phosphoric acid hydrogel, which also act as packaging materials. Two carbon nanotube (CNT) electrodes are twisted together to form a 1-D supercapacitor. The excellent tensile property of the capacitor guarantees a stable electrochemical performance (a capacity of 30.7 F g^{-1}) even after experiencing a 200% stretch. This kind of flexible energy device can be woven into two-dimensional flexible fabrics, which can be made into clothing, effectively serving as an energy-storing textile. However, when creating clothing from these materials, it's imperative to consider the biocompatibility between the fabric and the wearer's skin. A high level of biocompatibility is essential to protect the wearer's skin or body from potential inflammation and provide a comfortable wearing experience. At present, biocompatibility research mainly focuses on natural materials and non-biotoxicity, aiming to ensure the safety and comfort of users in wearable energy storage clothing.

1.2.2.2 Bendable and twistable properties of one-dimensional flexible batteries/supercapacitors

Bending aligns with a natural characteristic of 1-D flexible devices, where the ability to bend makes warp formation feasible. An impressive example in this realm was presented by Peng's group (Zhang et al., 2015). They reported a bendable 1-D hybrid lithium-ion battery, in which three different 1-D electrodes (lithium titanate, lithium manganate, and carbon) were twisted together (Figure 1.7c). The hybrid fiber battery achieved a high energy density of 50 mW h cm^{-3} or 90 W h kg^{-1} and a power density of 1 W cm^{-3} or 5970 W kg^{-1}. Accordingly, they also prepared a 1-D hybrid lithium-ion supercapacitor device, featuring lithium manganate and carbon electrodes. In comparison to 2-D electrodes, the 1-D multi-electrodes can be easily combined together. While the three 2-D electrodes need a lamination design, implying only two electrodes can close to each other. The flexible energy storage device offers an array of possibilities, as it can be bent and twisted into various configurations, making it highly adaptable to different application scenarios. The ease of integration and manipulation further emphasizes the potential of one-dimensional flexible energy devices for a wide range of practical applications. At present, the Peng group has successfully prepared 1D fiber batteries on a large scale using industrial equipment, and successfully woven this 1D fiber battery into cloth, achieving a huge upgrade from laboratory samples to industrial products.7,8 They creatively used metal wires as current collectors, effectively reducing the internal resistance of fiber batteries at ultra-long lengths, making it possible to industrially prepare and apply such batteries.

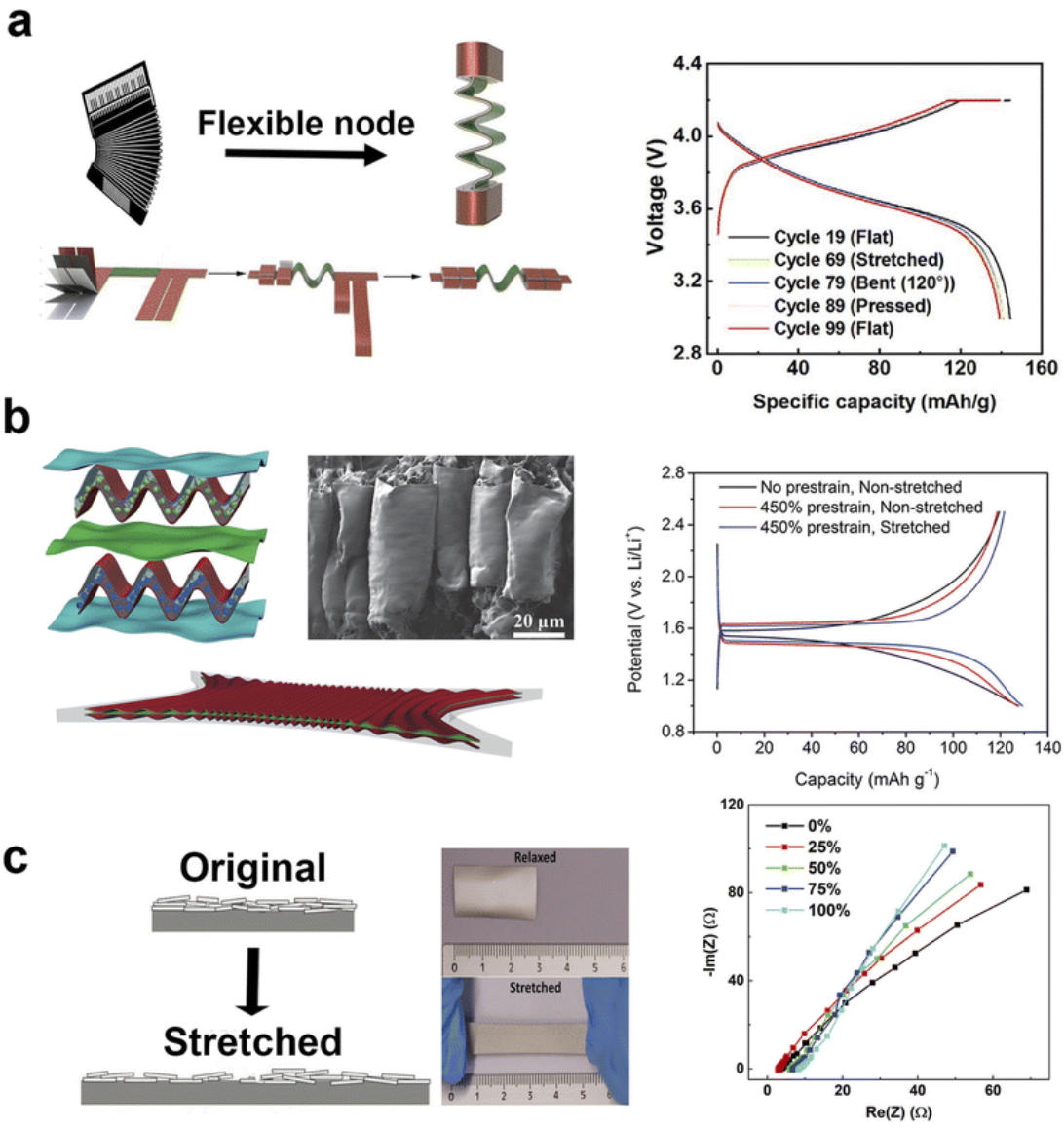
1.2.3 2-D flexible batteries/supercapacitors

2-D flat batteries represent one of the most prevalent forms of energy storage devices in use today (Arora et al., 2016). Generally, a 2-D flat energy storage device inherits a certain angle of bendability and torsion under a certain thickness, although stretching remains unattainable (Koo et al., 2012; Liu et al., 2013; Nam et al., 2015; J.-Z. Wang et al., 2009). In reality, due to requirement of a certain volume energy density, the devise is endowed with a limited length and width, resulting in a prescribed thickness. In order to meet the specific flexible energy storage systems, innovation is essential, whether through novel materials or advanced manufacturing processes. 2-D flexible devices necessitate compatible 2-D flexible electrodes, electrolyte/diaphragm, and packaging materials. Moreover, a 2-D electrode must exhibit stretchability,

torsional flexibility, and bending capabilities. The pursuit of such innovative 2-D flexible energy devices has the potential to usher in a new era of versatile and adaptable energy storage solutions, pushing the boundaries of what is achievable in practical applications.

Figure 1.8

Different stretchability of flexible batteries and their electrical properties.



Note. (a) Diagram of the structure of flexible accordion-like battery and corresponding charge and discharge curves of the battery in different states (Shi et al., 2019). (b) Schematic diagram, overall picture and scanning electron microscope image of arch electrode structure, and corresponding charge and discharge curves of the battery in different states (Weng et al., 2015). (c) Schematic drawings and century photos of high

elastic substrates with silver layers under normal and stretched conditions and their AC impedance curves.41 Panels reproduced with permission from (a) (Elsevier), (b) and (c) (Wiley).

1.2.3.1 Stretchable properties of 2-D flexible batteries/supercapacitors

Innovative manufacturing processes have paved the way for the development of highly elastic electrode substrate materials, enabling the realization of stretchable property in two-dimensional flexible batteries and supercapacitors. Yang's team (Shi et al., 2019) designed a stretchable accordion-like battery as show in Figure 1.8a. The intelligent design separates the energy storage part from the stretchable part, achieving both high energy density and stretchability simultaneously.

The as-prepared stretchable lithium-ion battery employed lithium cobalt oxide as the electrochemically active material and aluminum foil as the current collector in the cathode, graphite and copper foil collector in the anode. The cathode and anode were wound together with the diaphragm to form a coil. At the joint of the coil, a conductive material is made into an accordion shape, allowing the entire battery to stretch.

The electrodes can also be molded into a certain shape to facilitate stretchability. For instance, Peng and his team (Weng et al., 2015) created arch-shaped electrodes (Figure 1.8b). These electrodes comprise lithium manganate with carbon nanotubes and a highly elastic substrate as cathode, and lithium titanate with carbon nanotubes and the same elastic substrate as anode. The as-prepared cell can be stretched up to 400% without any electrochemical performance loss. Under the 400% stretch state, the battery could deliver a capacity of about 100 mA h g^{-1}. Another innovative approach involves the combination of elastic substrate and current collector. Niederberger's group(X. Chen et al., 2019) laid a layer of conductive silver nanosheets on a highly elastic substrate (Figure 1.8c). During stretching and retracting process, the silver nanosheets could connect to each other all the time, guaranteeing a stable electrical conductivity, thus a stretchable current collector. A high elastic and stretchable electrode can be formed by laying the active materials on the stretchable current collector. The silver nanosheets attached elastic substrate can be stretched to 100% with a low sheet resistance of about 2.7 Ω $\square^{-1}$.

In addition to these methods, active materials combined with graphene or carbon nanotubes offer a route to self-flexible electrodes. Such electrodes without current collector can be bent or twisted like paper. Ahn's group comprehensively explored the application of graphene-based active materials in flexible batteries, covering various types of graphene (Kim et al., 2021), including CVD-graphene, graphene flake, GO, rGO and graphene-based hybrid materials. In terms of carbon nanotube-based composite, Wei's group (Gu et al., 2017) reported a stretchable composite electrode of carbon nanotube and lithium manganate (LMO) and applied in lithium-ion batteries. The as-prepared cell could achieve 100% stretchability and maintain electrochemical properties simultaneously.

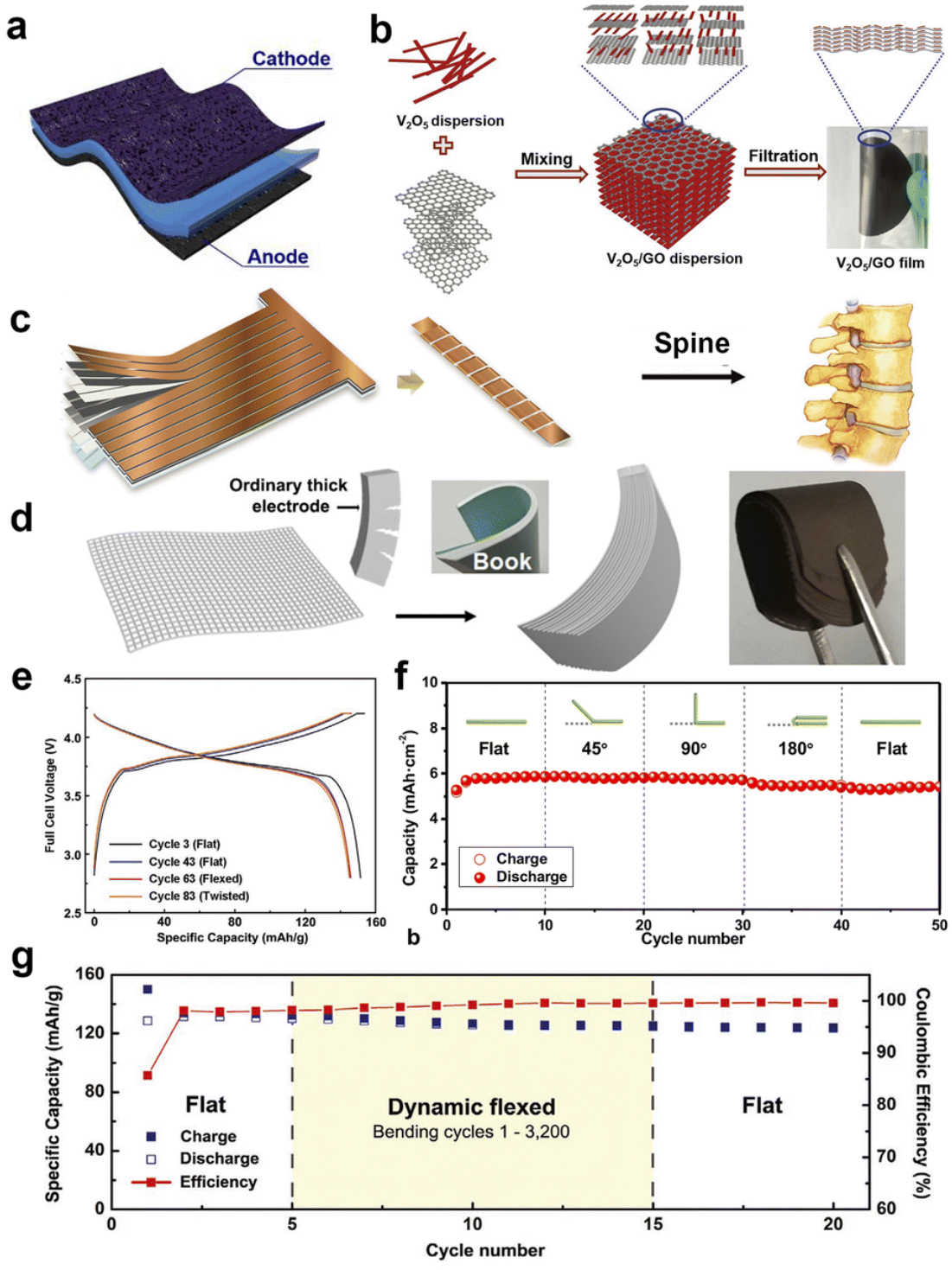
1.2.3.2 Foldable properties of 2-D flexible batteries/supercapacitors

The foldable properties of two-dimensional flexible batteries and supercapacitors are harnessed through the use of polymer materials known for their flexibility. For instance, the polymer materials can be applied as the substrate to support the active material, and in some cases, they can also act as both flexible substrate and electrochemical active material. Schubert's group (Hager et al., 2020) has systematically introduced and summarized the application of various polymer materials in flexible batteries. For example, polypyrroles (PPY), polythiophene (PT), poly(ethylenedioxythiophene) (PEDOT), and other alkoxy-sub-stituted polythiophene have been applied in various flexible batteries/supercapacitors due to their exceptional REDOX activities. While, these polymer materials have relatively low specific capacity (<100 mA h g^{-1}), they eliminate the need for binders as electrodes, resulting in a slight overall specific capacity increase. The elimination of an additional flexible substrate further enhances the overall specific capacity of flexible electrodes. As a flexible and cost-effective substrate, carbon cloth with is commonly used for flexible electrode substrates. Wu's group (Lie Ma et al., 2019) adopted carbon cloth and thermoplastic polyurethane (TPU) as conductive and flexible substrate to load the 3,4,9,10-perylenetetracarboxylic diimide (PDI) active material (Figure 1.9a). This innovative approach resulted in the creation of a foldable electrode with a specific capacity of about 120 mA h g^{-1}. Such foldable electrodes have been successfully applied in flexible lithium-ion battery, showcasing their ability to power LED light perfectly when bent at 180°. These developments highlight the promising potential of

foldable two-dimensional flexible batteries and supercapacitors for a wide range of applications.

Figure 1.9

Diagram and electrochemical performance of different flexible batteries/supercapacitors that can be bent or twisted.



Note. (a) Schematic diagram of an electrode with carbon cloth loaded active materials (Lie Ma et al., 2019). (b) Synthesis process of graphene oxide loaded vanadium pentoxide flexible electrode (Haiqing Liu et al., 2017). (c) A fabrication process of spine-like flexible electrode (Qian et al., 2018). (d) Schematic diagram of book-like flexible electrode preparation and (f) cycling performances (Huang et al., 2022). (e and g) Charge–discharge curves and cycling performances of a spine-like battery in different flexible states (Qian et al., 2018). Panels reproduced with permission from (a) (Elsevier), (b), (c), (e) and (g) (Wiley) (d) and (f) (Royal Society of Chemistry).

As mentioned earlier, the graphene demonstrates its versatility by forming composites with various materials, especially 2-D REDOX active materials, to create flexible electrodes. In 2017, Feng's group (Haiqing Liu et al., 2017) made an exciting advancement by combining graphene with vanadium pentoxide (V2O5) nanobelt to prepare flexible electrodes for symmetric supercapacitors (Figure 1.9b). The electrode was not limited to supercapacitors and could also function as a cathode in lithium-ion batteries. Both graphene and V2O5 exhibit 2-D sheet-like characteristics, and V2O5 readily attached on the surface of graphene layers, forming a 2-D flat and self-supporting electrode.

In addition to using flexible materials, innovative preparation methods can also make electrodes bendable and flexible. For example, in 2022, Wang's group simulated the bendable properties of books and produced book-like bendable flexible electrodes, which were successfully used in flexible lithium-ion batteries and sodium-ion batteries. Capacities of 5.88 mA h cm−2 and 5.24 mA h cm−2 were obtained in lithium-ion batteries and sodium-ion batteries. And the battery is used in smart insoles, flexible LED arrays and Android smart watches (Huang et al., 2022).

1.2.3.3 Twistable property of 2-D flexible batteries/supercapacitors

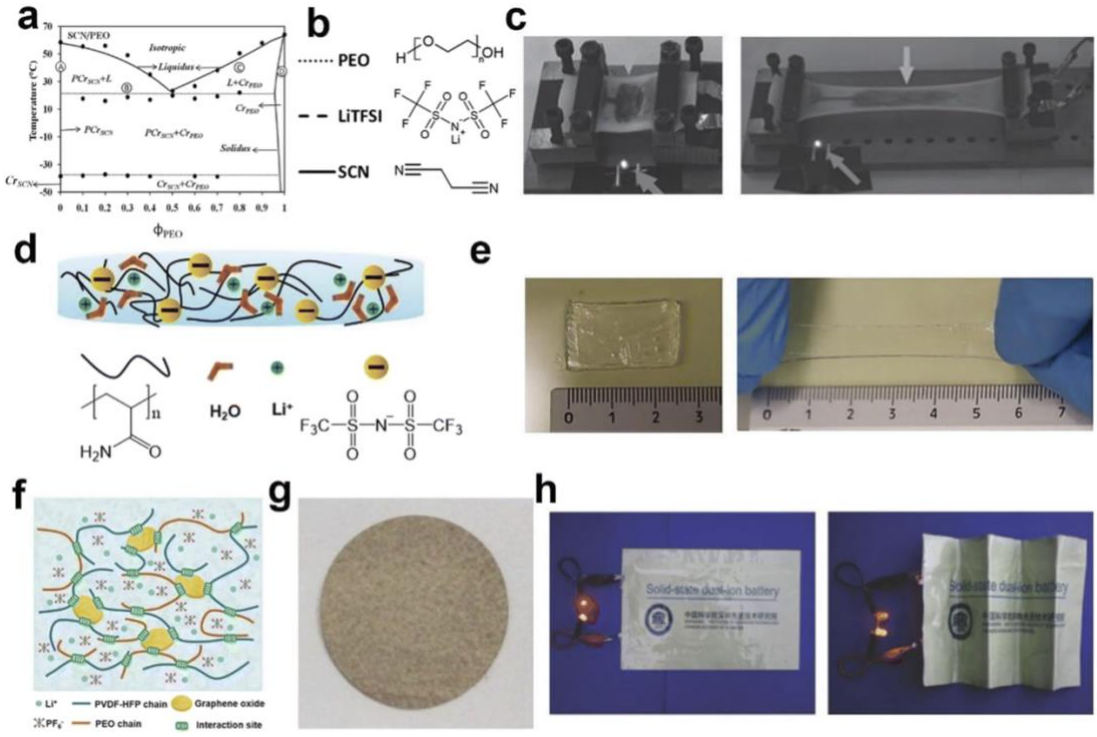
In general, while stretchable energy devices can typically be twisted, it's important to note that not all twistable energy devices are necessarily stretchable. Highly elastic materials, such as polymers, are frequently used in flexible batteries and their electrodes. However, these materials have lower power and energy density compared to traditional metal foil substrates. Innovation in the electrodes manufacturing process is an effective way solve the above issue. In terms of torsional electrodes, Yang's group (Qian et al., 2018) introduced a spine-like cell design with

multiple sections and small intervals between them (Figure 1.9c). When applied in lithium-ion batteries, the conventional lithium cobaltate (LCO) as cathode with aluminum foil as current collector and graphite as anode with copper foil as current collector. The as-prepared battery could maintain excellent capacity even when subjected to bending and twisting (Figure 1.9d). Notably, innovations in electrode and cell manufacturing processes hold great potential for practical implementation in flexible battery production by battery manufacturers.

1.2.4 Flexible electrolyte & diaphragm

Figure 1.10

Schematic diagram of various flexible electrolytes.



Note. (a) Binary phase diagram of the PEO/SCN mixture, and (b) chemical structures of the LiTFSI electrolyte (Echeverri et al., 2012). (c) The gel electrolyte was applied to the stretchable lithium ion battery, and the battery photos before and after the stretching (Weng et al., 2015). (d) Schematic illustration of the design concept of PAM-WiS gel electrolyte, and (e) photos of the unstretched and stretched electrolyte.41 (f) Schematic of the 3D porous polymer network, and (g) optical photographs of the dual-ion gel electrolyte, and (h) the electrolyte is applied to a bendable dual-ion battery, and

the battery photos before and after bending (Chen et al., 2018). Panels reproduced with permission from (a) and (b) (ACS Publications), (c)–(h) (Wiley).

Except electrodes, suitable electrolyte and diaphragm are critical components in the development of flexible batteries/supercapacitors. Gel electrolytes are commonly used in flexible energy devices, serving as both electrolyte and diaphragm (Li et al., 2019). Zhi's group (Longtao Ma et al., 2019) prepared a super stretchable gel electrolyte using sodium polyacrylate and cellulose. The gel electrolyte can be stretched as large as 800% in a 2-D cell and 500% in a 1-D fiber cell. Kyu's group (Echeverri et al., 2012) explored a polymer electrolyte with poly(ethylene oxide) (PEO), succinonitrile (SCN) (solid plasticizer) gels, and bis(trifluoromethane)sulfonimide (LiTFSI) as conductive salt (Figure 1.10a and b). This polymer electrolyte with excellent ionic conductivity and certain stretchability was subsequently applied in the flexible lithium-ion battery by Peng's group (Figure 1.10c) (Weng et al., 2015). Niederberger's group dispersed LiTFSI in polyacrylamide hydrogel and applied as both diaphragm and electrolyte.41 Specifically, acrylamide monomer and ammonium persulfate were dissolved in water initially, and then obtained the polyacrylamide hydrogel via a polymerization process. After that a high concentration of LiTFSI aqueous solution was added and comprehensively stirred to prepare the flexible gel electrolyte. The as-prepared gel electrolyte inherits wide working voltage window, high elasticity and high ionic conductivity, as shown in Figure 1.10d and e.

The resulting flexible dual-ion cell could be folded freely. Additionally, cells utilizing the gel electrolyte, often referred to as solid-state batteries, are safer than their liquid electrolyte counterparts due to the gel's high operating voltage and temperature. In addition to conventional energy devices, gel electrolytes find utility in flexible dual-ion batteries. These environment ally friendly and cost-effective devices have high voltage and show promise in the realm of flexible energy devices. In 2018, a dual-ion gel electrolyte (Figure 1.10f–h) was prepared by copolymerizing poly(vinylidene fluoride-hexafluoro propylene)(PVDF) with poly(ethylene oxide)(PEO) and then incorporating graphene oxide(GO) (Cao et al., 2023; Chen et al., 2018; Wu et al., 2024; Zhang et al., 2024). The electrolyte featured an abundance of 3D channels, facilitating the rapid movement of conductive ions. The resulting flexible dual-ion cell could be folded arbitrarily. Moreover, cells made with the gel electrolyte, also known as solid

state batteries, are safer than their liquid electrolyte counterparts due to the relatively high operating voltage and high operating temperature of the gel electrolyte.

1.2.5 Flexible packaging materials

A flexible packaging is essential for isolating the interior components of a battery or capacitor from the surrounding environment. In certain prototype energy storage devices, gel electrolyte can even play the role of packaging material. For instance, some 1-D flexible energy devices lack traditional packaging and consist only electrodes and gel electrolyte.87 Some traditional materials, such as aluminum plastic film, are often used as packaging materials for the lithium-ion battery. The aluminum plastic film is composed of two layers of polymers and an aluminum foil in between, which can be bent and twisted. Through the above-mentioned new techniques, such as accordion-like and spine-like production processes, the aluminum-plastic film can also inherit the stretchable property. Other flexible polymers, such as polystyrene, polydimethylsiloxane (PDMS), and silicone rubber, are suitable choices for packaging. In flexible energy devices, packaging materials not only serve the purpose of environmental isolation but must also possess flexibility. Therefore, many packaging materials with the above-mentioned characteristics have potential to be applied in soft energy devices.

1.2.6 Conclusions and outlooks

In this perspective, we systematically overview the 1-D and 2-D forms flexible energy devices, taking into account various types of flexibility, including bending, twisting and stretching. We also delve into the essential components of these devices, including flexible electrodes, electrolyte/diaphragm and packaging materials. A comparative analysis of typical flexible batteries/supercapacitors are summarized in Table 2, highlighting their electrode characteristics, electrolytes, diaphragms, packaging materials, flexibility types, and bending performance.

Generally, the flexible electrodes with elastic substrates or special flexible nodes behave a lower energy density compared with non-flexible counterparts. Traditional metal foil can only be bent or distorted to a certain extent; thus, a high-elastic substrate is critical to obtain a flexible electrode that can be bent, twisted and stretched.

Compared to traditional liquid electrolytes and polymer membranes (e.g., PE, PP), the gel electrolyte is more widely used in flexible batteries/supercapacitors due to its natural flexible and ionic conductive properties. After dissolving salts, the gel electrolyte has the ionic conductivity as an electrolyte, and separates electrodes as a diaphragm. The packaging material is required to separate the inside of the device from the outside environment. In flexible energy devices, it must be endowed with flexibility as well.

Despite some significant progress made in flexible energy storage devices, there are still many challenges need to be overcame. Thus, the current challenges and prospective research focus in this field are summarized as follows:

The issue of reduced electrochemical performance after deformation is a critical concern. Adding conductive carbon materials into substrates or using conductive polymers are effective way to alleviate the performance loss of the distorted electrode. While the low density of polymers and carbon materials would reduce the power and energy density. Novel electrode fabrication processes, such as adding flexible nodes to the electrodes, could realize an improved volumetric power and energy densities compared to soft substrates. However, the conventional materials and current collectors tend to be unstretchable more or less, making it crucial to simultaneously enhance the power density, energy density and flexibility in electrodes for future research.

Similar to the elastic substrate, the gel electrolyte also behaves a low density. At present, the gel electrolyte displays the thickness of few hundred microns to a millimeter, which greatly affects the device volume energy density and power density. However, reducing the thickness of gel electrolyte may risk internal short circuit, especially in stretched state. Therefore, the development of ultra-thin and flexible solid-state electrolytes emerges as a promising avenue for future research.

Moreover, attention to flexible packaging material is also essential. Because the flexible packages are typically composed of polymers, research efforts in producing ultra-thin polymer materials hold promise in this field.

Chapter 2: A book-like organic based electrode with high areal capacity for high performance flexible lithium/sodium-ion batteries

2.1 OVERVIEW

By directly bonding the monolayer organic based electrodes together to assemble the book-like multilayer electrode, increased areal capacity and high flexibility can be achieved. The electrodes represent 5.88 mA h cm^{-2} at 0.7C and 5.24 mA h cm^{-2} at 0.2C areal capacity in lithium-ion and sodium-ion batteries, respectively.

2.2 BACKGROUND

Flexible batteries with high areal capacity have numerous advantages in powering all kinds of wearable electronic devices (Gaikwad et al., 2015; Nishide & Oyaizu, 2008; Park et al., 2019). Many wearable devices, such as smart insoles, skin displays and skin sensors, are often attached to human body parts (Stefana et al., 2021). These devices need to be flexible as the body parts change or move. As a power source of these devices, the study of the flexibility and high capacity of the battery is very important. Recently, organic electrode materials have attracted attention owing to their excellent sustainability and adjustable composition (Huang et al., 2021; Yin et al., 2020). Typically, organic materials are more suitable for flexible batteries because of their controllable synthesis and lower toughness than traditional inorganic electrode materials.1 However, the research on high areal capacity flexible electrode is rare because the limited electronic/ionic mobility in bulk organic materials (Fratini et al., 2020). Thus, it is critically important to improve the electronic/ionic dynamics in organic materials. Traditional linear batteries and ultrathin single-layer batteries have demonstrated sufficient flexibility, but with low areal capacity (Koo et al., 2012; Qian et al., 2018). Thick single-layer batteries tend to lose their flexibility and break easily in the process of bending (Wan et al., 2019; Yao et al., 2021). Flexible and thick single-layer batteries, which rely on new substrate, electrode and binder materials, often

sacrifice their areal specific capacity. The flexible cells produced by the new process increase energy density (Qian et al., 2018), but can only be flexible at a limited number of nodes. Therefore, it is a promising direction for researchers to design a thick electrode with high areal capacity and flexibility and apply it to batteries (Huang et al., 2020).

2.3 BOOK-LIKE ORGANIC BASED ELECTRODE AND BATTERIES

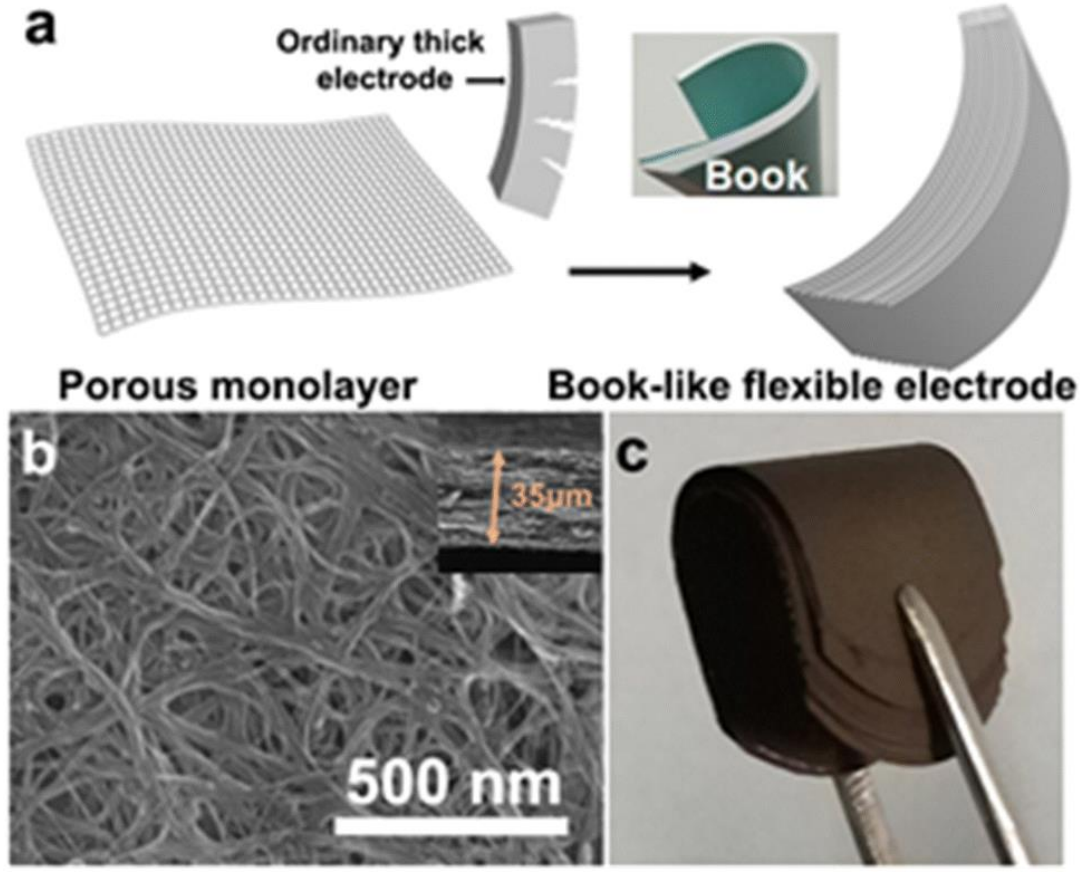
In this work, we rationally design an organic (3,4,9,10-perylenetetracarboxylic diimide, PTCDI) based composite by combining organic active material with high conductive carbon nanotubes, which present highly electronic/ionic mobility and excellent flexibility. Afterward, a book-like electrode can be packed by gluing multiple monolayered flexible electrodes, leading to an extremely high areal mass loading, thereby achieving outstanding areal performance for free-standing lithium/sodium ion batteries.

Compared with single-layer paper, book has thicker structure and can be bent, which provides an idea for improving areal capacity and realizing flexibility of electrode. The active material was PTCDI, a common organic cathode material, which REDOX reaction mechanism is a two-electron reaction (Figure 2.6) with a theoretical specific capacity of 136.6 mA h g^{-1}. Single-walled carbon nanotubes (SCNT) were used as a conductor and current collector to make porous, flexible monolayer electrodes without binder and metal foil. The thick book-like electrode (Figure 2.1a), consisting of a suitable number of porous monolayers, achieves a multiple capacity of the monolayer electrode. The spine of the book-like electrode, as the only fixed edge in the four sides (Figure 2.5a), connects all the monolayers to achieve the bending flexibility of the entire electrode, and acts as the place where the current is concentrated in and out (Figure 2.5b). This method can not only be used to make square flexible electrode, but also can be used in round or other shapes of flexible electrode (Figure 2.5c). The porous monolayer electrodes (Figure 2.1b) are integrated together in a book-like manner as a multilayer, flexible (Figure 2.1c) and thick electrode (Figure 2.5e). As the layers are the same pole, the possibility of internal short circuit is eliminated. The porous layers can make the ion transfer between layers unimpeded in the radial direction after making the multilayer book-like electrode (Figure 2.5b). Due to the presence of aluminium foil and copper foil in the middle of the traditional electrode, ions cannot penetrate, so it can only be used as a single layer

electrode, and the cathode and anode are stacked in a staggered manner. This method is limited by the separator side zigzag continuous placement, and the head pole lug welded together, so that the head and two sides of a total of three edges are fixed, it is difficult to achieve flexibility (Fig S1d, ESI†). Although a few layers of cathode and anode interlaced, the bending flexibility can be maintained to a certain extent, but the internal battery is easy to be damaged while bending (Wang et al., 2014).

Figure 2.1

Images of book-like electrode



Note. (a) Schematic diagram of preparation of book-like flexible electrode by porous monolayer electrode. (b) SEM images of porous monolayer electrode, and the small SEM image shows a cross-section with a thickness of about 35 μm. (c) Bent photo of book-like flexible electrode.

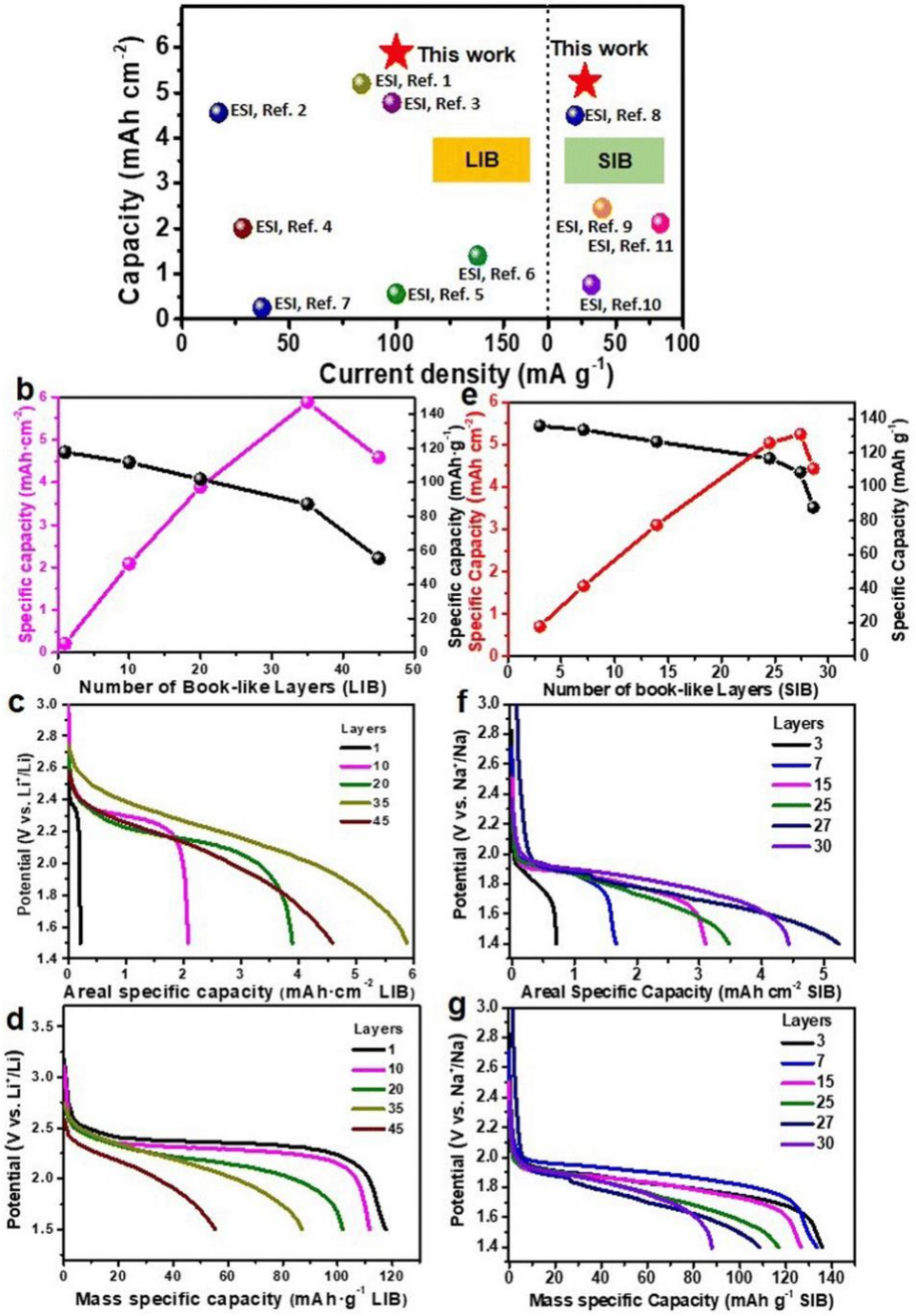
The porous monolayer electrode, composed of organic materials and carbon nanotubes, avoids metal contamination when discarded. Organic materials, especially those with large π structures, are combined with carbon nanotubes through π–π

interactions (Fukushima et al., 2003; Segawa et al., 2016; Yang et al., 2017). The π–π interaction not only improves the conductivity between the electrode material and the carbon nanotubes, but also avoids the use of binders such as PVDF. The capacity of organic materials comes from their own REDOX groups, adsorbing and desorbing metal cations during charge-discharge reactions. Compared with layered inorganic materials, its application field is less affected by cation radius. Therefore, the electrode can be widely used in lithium-ion batteries, sodium-ion batteries, and even zinc-ion batteries.

We tested the areal capacity of book-shaped electrodes with different layers in lithium-ion batteries and sodium-ion batteries, to verify the effect of this electrode fabrication method on the improvement of areal capacity and explore the best layer numbers. The single-layer electrode was then made into multilayer book-like electrode with different number of layers, and obtained a good areal capacity between both two types of batteries (Figure 2.2a and Table 3). The electrodes were first investigated in lithium-ion batteries. We tested the areal specific capacity of monolayer electrode, 0.21 mA h cm^{-2}, and then prepared 10, 20, 35 and 45 layers electrodes. The areal capacities are 2.08, 3.89, 5.88 and 4.58 mA h cm−2 respectively (Figure 2.2b), which are 9.9, 18.5, 28 and 21.8 times of monolayer electrode. All these tests were performed at a current of 0.7C (0.1 A g^{-1}). We can see from the number of multipliers, within 10 layers, the areal capacity is almost multiplied increased without loss. Between 10 and 20 layers, the capacity is slightly lost as the multiplied increase. The number of layers with the highest areal capacity is 35. Although the capacity of each layer has a certain loss relative to 35 times of single layer, the obtained areal capacity is the highest. After 35 layers, the capacity provided by each layer is greatly reduced and the actual total areal capacity begins to decrease.

Figure 2.2

Data of book-like electrode batteries



Note. (a) Comparison of specific areal capacity of book-like electrode in flexible LIB and flexible SIB with other work. (b and e) Areal specific capacity and mass specific capacity of book-like electrodes with different layers in LIB and SIB. (c–g) Galvanostatic discharge curves of lithium-ion batteries (c and d, 1.5 V cut-off voltage vs. Li+/Li) and sodium-ion batteries (f and g, 1.4 V cut-off voltage vs. Na+/Na) with different layers.

In the galvanostatic discharge curves of lithium-ion batteries with different layers, it can be seen that with the increase of layers, the discharge platform gradually decreases and the polarization effect becomes higher and higher (Figure 2.2c). This property is more obvious in the mass galvanostatic discharge curves (Figure 2.2d). From monolayer to 20 layers, a clear platform can be maintained from the discharge curve. When the number of layers increases to 35 layers, the platform can still be observed, but shows a diagonal line falling. At the last stage of discharge, the slope becomes steeper, indicating that the discharge process is completed. It is difficult to see the platform of the 45-layers electrode, indicating that the battery polarization has increased to a certain extent, affecting the utilization rate of the active material of the entire electrode. The mass specific capacities of the electrodes with different layers are 117.6 (1 layer), 111.7 (10 layers), 101.8 (20 layers), 87.1 (35 layers) and 55.3 (45 layers) mA h g−1, respectively (Figure 2.2c). If the active material effective utilization rate of single layer electrode is 100% as a reference, the effective utilization rate of 10, 20, 35, 45 layers electrode is 95.98%, 86.56%, 74.06%, 47.02%. Since the efficiency is related to the cost of the entire battery, 10 to 20 layers may also be a good choice for LIB manufacturers from both cost and areal capacity considerations. The capacity of the book-shaped electrode in the sodium-ion batteries was also studied, to verify whether the capacity of electrode still maintained the multiplied rate of increase. The areal specific capacitance and mass specific capacitance data of different layers were obtained at 0.2C (27.32 mA g−1) discharge current. We tested 3, 7, 15, 25, 27 and 30 layers of electrodes and obtained areal capacities of 0.71, 1.67, 3.11, 5.04, 5.24 and 4.43 mA h cm−2 respectively. As can be seen from the line chart (Figure 2.2e), when the number of layers is less than 25, the areal capacity almost presents a straight line, indicating that the capacity increases almost multiped with the increase of the number of layers. The slope of the increase decreases when it increases from 25 layers to 27 layers, but it still reaches the maximum value of 5.24 mA h cm−2. After 27 layers, areal specific capacity decreases. We can see from the galvanostatic discharge curve, when the layer number is less than 15, the difference between platforms is small and the polarization effect is tiny (Figure 2.2f and g). Beyond 25 layers, the discharge platform becomes more inclined, and the polarization effect of the electrode at this time in sodium-ion batteries becomes strong. Finally, at the 30 layers, the areal capacity of the entire electrode begins to decrease due to the excessive polarization effect. The mass specific capacities of layers 3, 7, 15, 25, 27 and 30 are 135.9, 133.6,

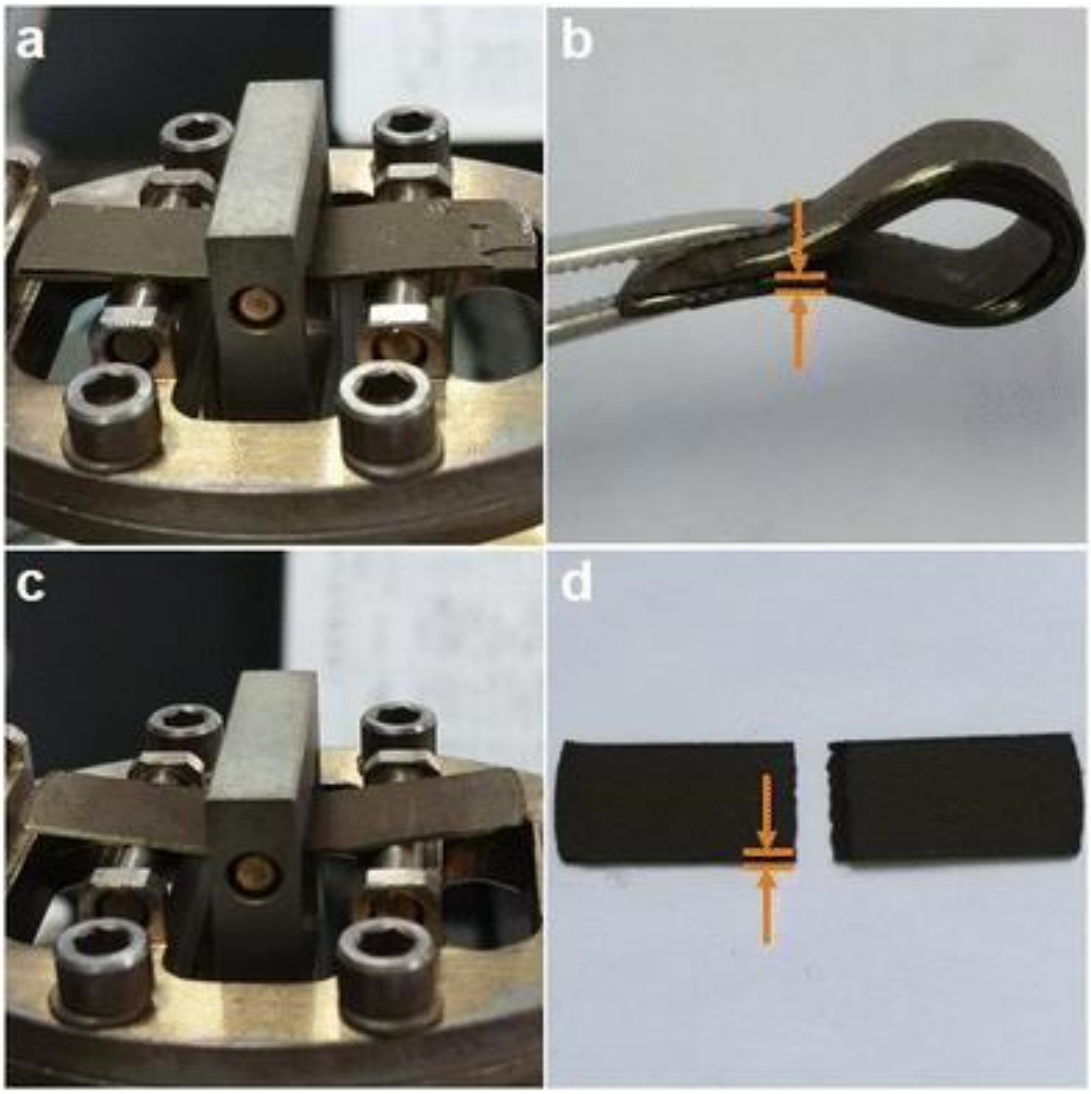
126.6, 116.8, 108.7 and 87.9 mA h g−1 respectively. If the theoretical capacity of the active material (136.6 mA h g−1) is calculated as 100% utilization rate, the rate of the electrode with different layers is 99.5% (3 layers), 97.8% (7 layers), 92.7% (15 layers), 85.5% (25 layers), 79.6% (27 layers) and 64.3% (30 layers). The cost advantage of sodium-ion batteries and high utilization rate of active material make the cost advantage of book-like electrode further improve. Although the electrode with 27 layers has the highest areal specific capacity, the electrode with 25 or less layers has a higher cost advantage. Combining cost with capacity data, 25 layers may be the best choice for some SIB manufacturers.

Cyclic voltammetry (CV) curves can be obtained from supplementary documents, with a cathode reduction peak of around 2.06 V at discharge and an oxidation peak of around 2.98 V at charge in LIB (Figure 2.7a). The CV curve of the sodium-ion battery is also available in the ESI† (Figure 2.7b). Due to the large radius of sodium ion, except for the first discharge, the two-electron REDOX reaction in the charging and discharging process has two oxidation peaks and reduction peaks respectively, indicating that the discharge process and the charging process are composed of two steps.

The book-like electrode has excellent bending flexibility, while the ordinary thick non-book electrode is very easy to break during bending. To test this idea, we performed a three-point bending test on both electrodes (Figure 2.3a and c, the two electrodes have the same mass and size, and the thickness is about 1.2 mm, Figure 2.3b and d). During the bending test, with the relative displacement of the central stress point to the two side support points, from the beginning (flat shape, Figure 2.3a) to the end of the test (approximately 180 degrees bending), the book electrode consistently exhibits stress of less than 0.01 N (Figure 2.8), which is below the minimum testable value of the instrument. The conventional thick electrode of the same mass shows a maximum stress of 0.50 N when tested. When the bending angle is 20 degrees, the stress value of the thick electrode begins to shake, indicating that the electrode begins to break. When the bending angle reaches 32 degrees, the stress decreases rapidly and the electrode completely breaks (Figure 2.8). After the test, the book-like electrode is not damaged (Figure 2.3b and Figure 2.10a, b), while the normal thick electrode breaks into two parts (Figure 2.3d).

Figure 2.3

Electrode mechanical test



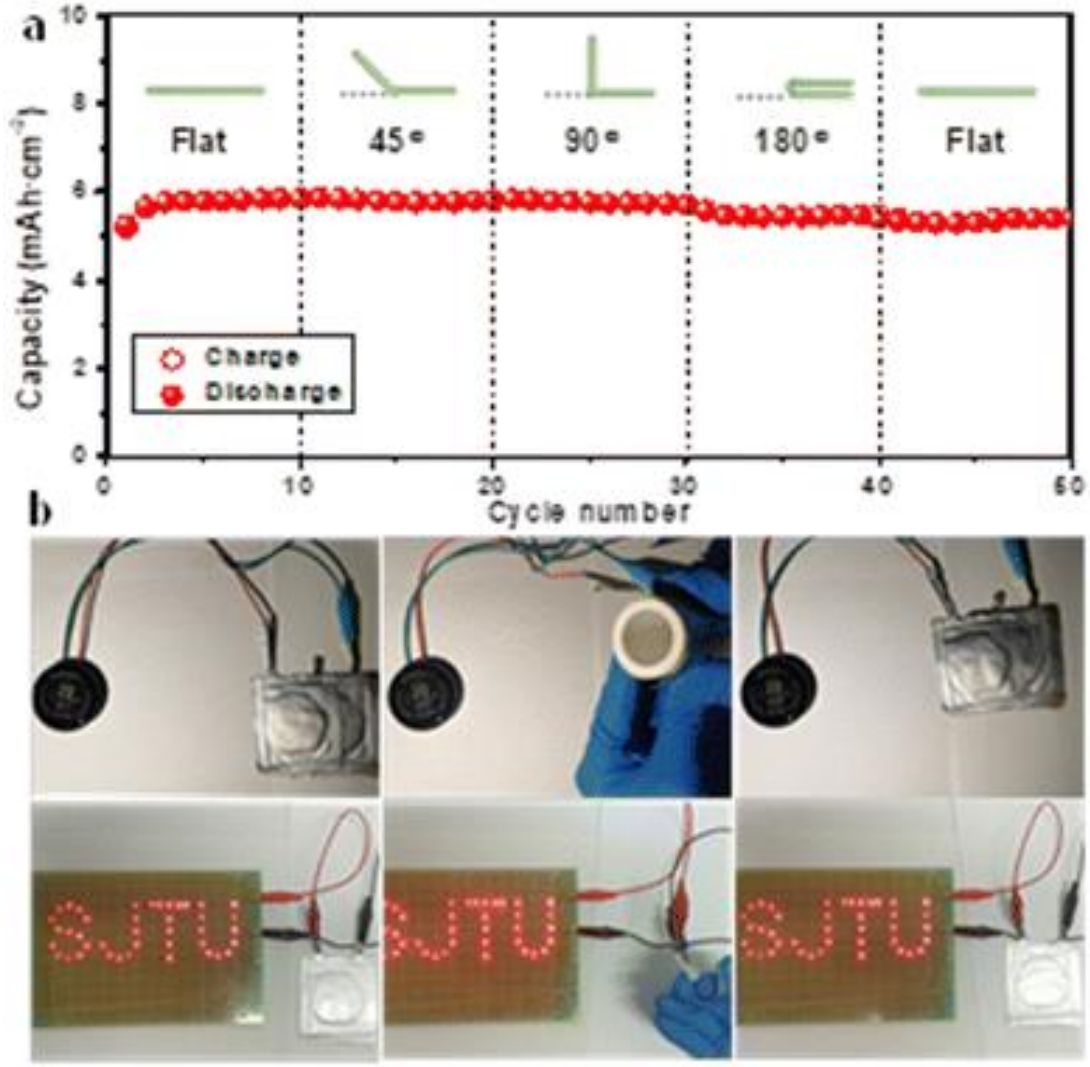
Note. (a and b) Images of book-like electrode before (a) and after (b) three-point bending test. (c and d) Images of conventional thick electrode of the same mass as book-like electrode before (c) and after (d) three-point bending test.

We calculated the fracture bending angles of electrodes with different thickness (Figure 2.9a) and the calculation process is in the 2.4. The stretching curve of the single-layer thin electrode was tested (Figure 2.9b), and it is assumed that the elongation at break of the electrode is the same under different thicknesses. As electrodes are bent, the stretch of outside region of the electrodes will overtake that of inside, leading to the break of electrode (Figure 2.9c). The fracture bending angle simulated (30.8 degrees) by the thick electrode is similar to the actual value (32

degrees). After calculation, when the thickness of electrode is less than 59.8 μm, the fracture angle is more than 180 degrees, which is the max angle a flat plate folds, and the thicker the electrode is, the smaller the angle is. The thickness of our single-layer electrode prepared is generally about 35 μm, far less than 59.8 μm, and its fracture bending angle is 308 degrees, more than 180 degrees. Book-like electrodes, which consist of several layers of monolayer electrodes, inherit the bending properties of monolayer electrodes and do not break beyond 180 degrees bending.

Figure 2.4

Battery flexibility and charge discharge performance in the bent state



Note. (a) The areal capacity change of the flexible battery in the bending test. (b) On the top is the flexible battery that powers the smartwatch, and bottom is the LED array, and from left to right are the photos before, during and after bending operation.

Flexible pouched lithium-ion batteries made from the electrodes were tested for bending-electrical properties. The maximum areal capacity before bending is 5.86 mA h cm^{-2}, and when bending 45 degrees, the capacity still remains at 5.77–5.86 mA h cm^{-2}. During 90 degrees, the capacity is maintained at 5.74–5.85 mA h cm^{-2}, and 180 degrees, the capacity is maintained at 5.45–5.58 mA h cm^{-2}. When the flat shape is restored, the capacity remains at 5.30–5.43 mA h cm^{-2} (Figure 2.4a, all tested at 0.7C). The galvanostatic charge-discharge curves of the battery at different bending angles have no obvious abnormality (Figure 2.10). Then we applied the battery to a Huami smart watch and a LED array (Figure 2.4b). Both the watch and the LED array can work normal before, during and after the bending test. In addition, this kind of battery is also tested in a smart insole, wearable LED arrays (Figure 2.11), and can provide normal power supply to the devices before, during and after bending.

In summary, a flexible multilayer book-like electrode was first prepared by referring to nature and applied in flexible lithium-ion batteries and sodium-ion batteries. The combination of PTCDI with SCNT avoids the use of binders such as PVDF. Furthermore, the π–π interaction between PTCDI and carbon nanotubes enhances the conductivity, thereby achieving a high electron mobility. The porous layered structure provides channels for the radial movement of ions between layers, and the silver paste spine has good electrical conductivity, making electrons not only easily move within the layer, but also easily pass through the spine into and out of the electrode. With this sophisticated structure, the specific areal capacity can be increased multiplicatively, reaching 5.88 mA h cm−2 (LIB) and 5.24 mA h cm−2 (SIB), under the premise of flexibility. Also, we quantified and calculated the bending flexibility of the electrodes, and successfully applied them in lithium-ion battery and sodium-ion battery. This strategy of designing high areal capacity electrode can be also extended to utilize organic electrodes in many other flexible battery devices.

2.4 SUPPORTING INFORMATION SECTION

2.4.1 Preparation of porous single layer electrode

Take 21 mg PTCDI (3,4,9,10-Perylenetetracarboxylic diimide) and 9 mg single walled carbon nanotubes and place them in a beaker. Then pour in 100ml of ethanol solution. The beaker was then ultrasound for 6 hours. At the end of the ultrasound, the

mixed solution is pumped to form a membrane. The membrane was placed in the oven and vacuum dried at 70 oC for 12 hours.

2.4.2 Preparation of batteries

Areal specific capacity test using 2032 coin cells. Multiple single-layer electrodes are used directly for the cathode and no paste is required. The anode uses lithium or sodium metal. The book-like electrodes are fabricated from single-layer porous flexible organic electrodes. Coat one side of the monolayer electrode with silver paste, then attach the other monolayer electrode, and repeat until the number of layers reaches the target number (Figure 2.5e). Note that all monolayer electrodes can only be glued to the same side, otherwise the flexibility will be lost. Then, the multi-layer electrode was placed in an oven at 70 oC for 1 hour to form a thick, multilayer, flexible book-like electrode. The pouched pack battery fabrication uses the book-like flexible as cathode, carbon cloth embedded with lithium as anode.

2.4.3 Bending Angle calculation

Outside length = L_1, inner side length = L_2, the thickness of the electrode = d, bending angle = θ. See Figure 2.9c for other parameters.

$$L_1 = 2l_1 + al_1,\ al_1 = 2\pi r\frac{\theta}{360°}$$

$$L_2 = 2l_1 + al_2,\ al_2 = 2\pi(r+d)\frac{\theta}{360°}$$

If the electrode does not break when bent, then

$$L_2 - L_1 \le 0.094L_1$$

$$al_2 - al_1 \le 0.094L_1$$

$$\frac{\pi\,\mathrm{d}\theta}{180^{\circ}} \le 0.094L_1$$

When the three-point doing bending test, L_1 is 2 cm (instrument parameters).

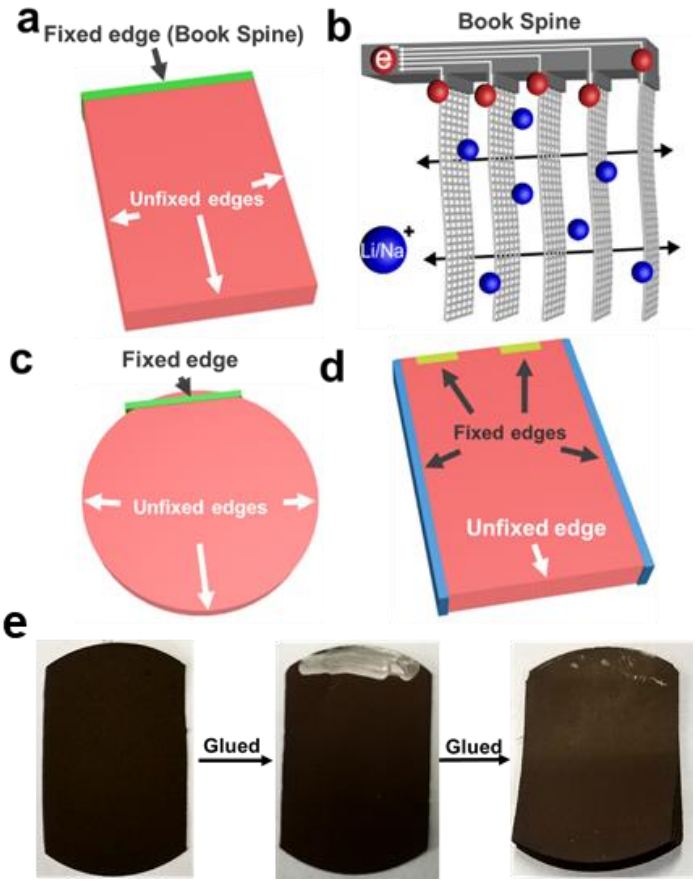
$$\frac{\pi\,\mathrm{d}\theta}{180^{\circ}} \le 0.188\ \mathrm{cm}$$

$$\mathrm{d}\theta \le 0.188\mathrm{cm} \times \frac{180°}{\pi}$$

When $\theta = 180°$, $\mathrm{d} \le 0.0598$ cm

Figure 2.5

The flexibility, detail and fabrication method of book-like electrodes, compared with conventional commercial electrode.



Note. (a) Fixed edge and three free edges of the book-like electrode. (b) The movement of electrons on the book-like electrode and the movement of lithium ions or sodium ions between the porous multilayer electrode in the radial direction. (c) The fabrication method of book-like electrode is applied to the flexible circular multilayer electrode. (d) A conventional cathode-anode alternating stack cell, with the sides fixed by a zigzag separator (blue) and the head fixed by lugs welding (yellow). (e) Pictures of the book-like electrode made of conductive silver paste bonded layers.

Figure 2.6

Two-electron REDOX reaction mechanism of PTCDI in LIB & SIB.

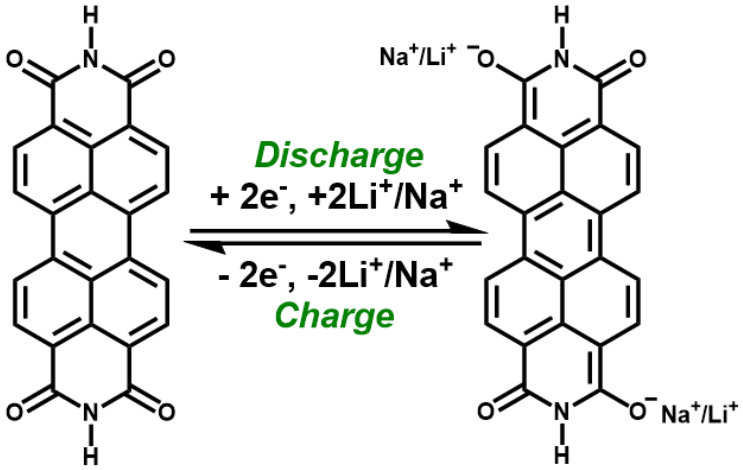


Figure 2.7

CV of book-like electrode in LIB (a) & SIB (b).

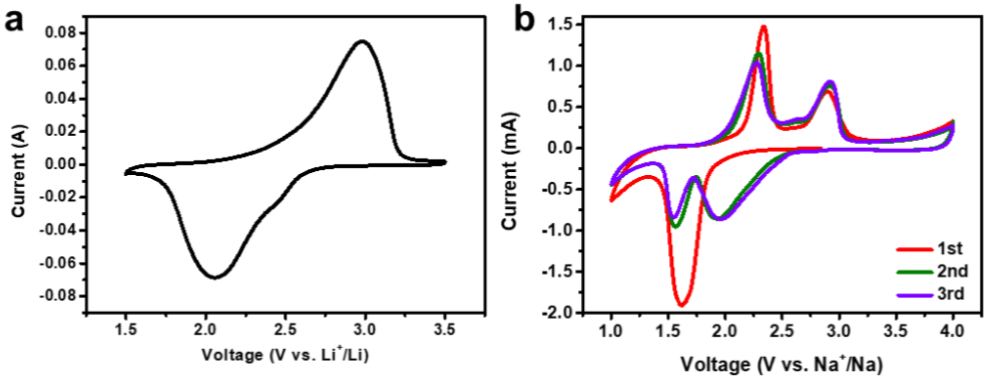


Figure 2.8

Force curves of two electrodes in three-point bending test.

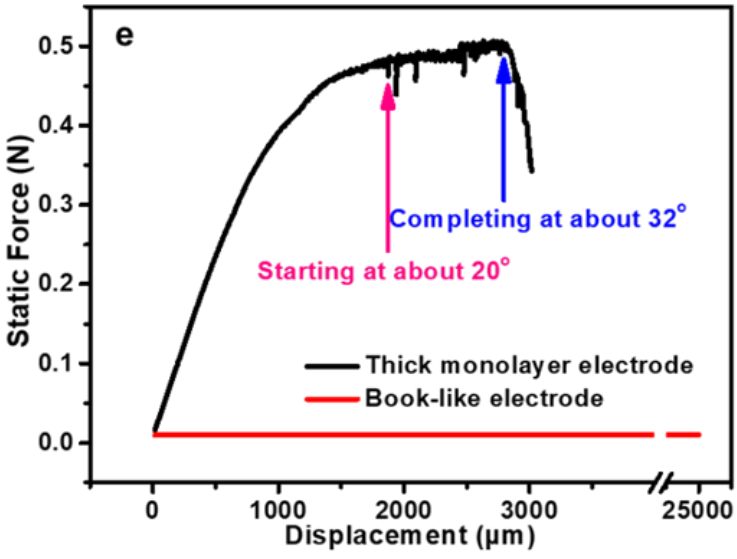
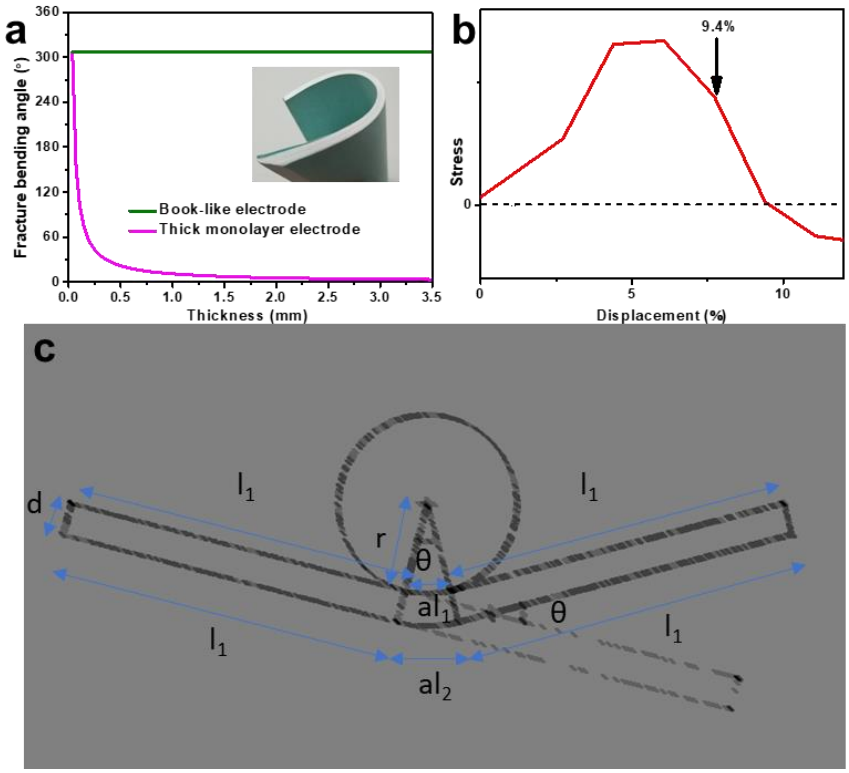


Figure 2.9

Calculations



Note. (a) The fracture bending angles of electrodes with different thickness. (b) Tensile fracture stress-strain diagram of the electrode. (c) Length parameters of each part when the electrode is bent.

Figure 2.10

Galvanostatic charge-discharge curves of flexible book electrode in bending test of lithium-ion battery

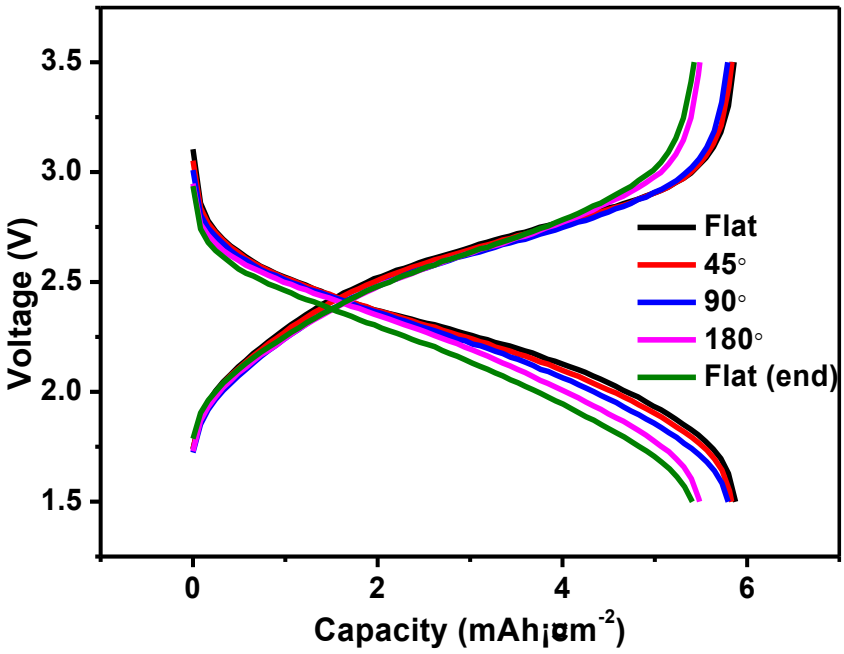


Figure 2.11

From left to right are photos of flexible batteries applied in a smart insole and wearable LED arrays.

Chapter 3: Pioneering Uniaxial Fiber Batteries: Structural Innovation for Enhanced Performance in Wearable Electronics

3.1 OVERVIEW

In recent years, fiber batteries have evolved from laboratory prototypes to industrial products with kilometer-scale lengths, enabling their integration into fabrics via industrial assembly lines. Traditional fiber batteries, composed of two or more fiber electrodes, suffer from performance issues due to inconsistent electrode surface distances, affecting rate discharge and cycle life. To address these issues, we designed an advanced uniaxial fiber battery (UAFB) that combines the structural integrity of planar batteries with the morphological advantages of fiber batteries. The UAFB design ensures constant close contact between the cathode and anode, preserving the separator's thickness and maintaining a face-to-face electrode structure throughout the active area, thereby optimizing electrochemical reactions. This innovation retains the flexibility and integration potential of fiber batteries, making it ideal for fabrics and wearable electronics. Compared to traditional bifilar fiber batteries, the UAFB exhibits superior charge and discharge capacities at various current densities, underscoring its enhanced performance and practical application value.

3.2 BACKGROUND

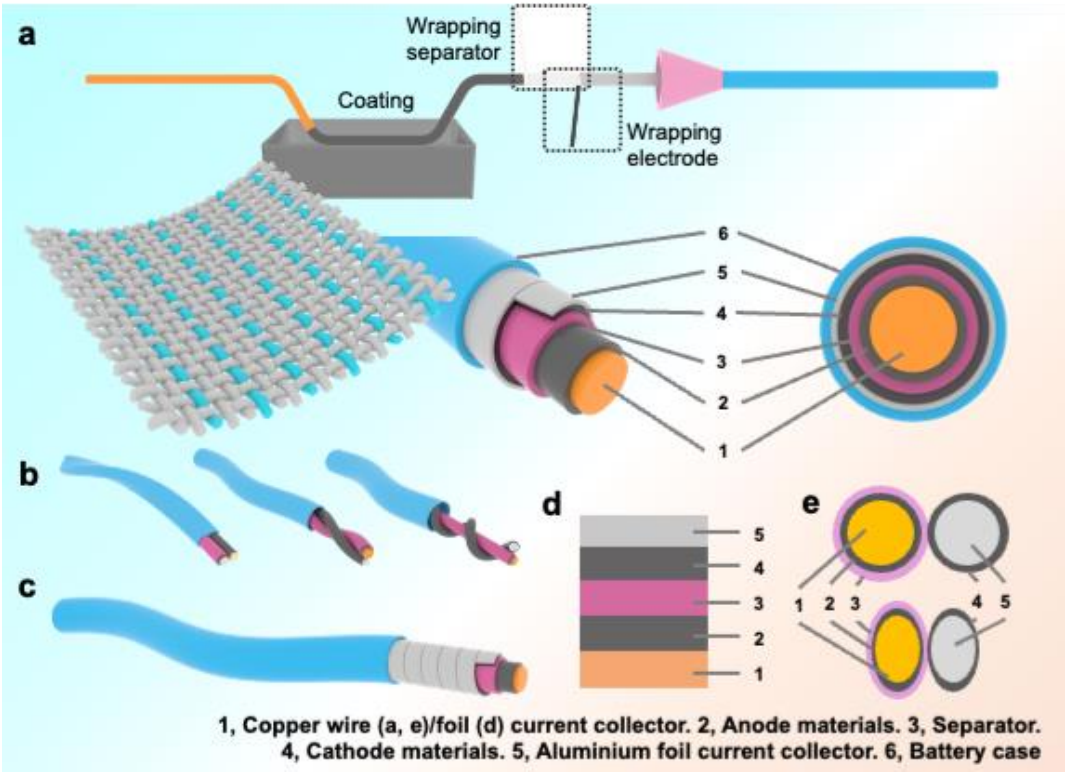
Flexible batteries have been extensively studied for their versatile application. Among them, one-dimensional flexible fiber batteries stand out for their ability to seamlessly integrate into two-dimensional flexible batteries, which in turn can be stacked to create flexible three-dimensional batteries (He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, Zhang, et al., 2021; J. Lee et al., 2020; Liao et al., 2022; C. Lu et al., 2024; Mo et al., 2020; Pu et al., 2024; L. Wang et al., 2020; Y. Zhou et al., 2020). These fiber batteries can be woven with traditional fibers to produce energy storage textiles (He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, Zhang, et al., 2021; Liao et al., 2022; C. Lu et al., 2024), adding functionality to clothing while maintaining comfort and breathability. These textiles find applications in wearable energy storage

products and power wearable electronic devices, driving the advancement of wearable electronics (Fu et al., 2017; Liu et al., 2018; Sun et al., 2013; Yang et al., 2024; Zamarayeva et al., 2017). Additionally, fiber batteries can be woven into all-fiber battery fabrics to meet the demands of wearable applications requiring high energy and functional density.

3.3 FIBER BATTERY WITH NEW STRUCTURAL DESIGN

Figure 3.1

Comparison of coaxial fiber batteries and traditional fiber batteries.



Note. (a) Schematic and structural diagram of the uniaxial fiber battery. (b) Traditional biaxial fiber batteries, including parallel biaxial, coiled biaxial, and a variant of the coiled biaxial. (c) Uniaxial fiber battery. (d) Cross-sectional diagram of the planar battery. (e) Cross-sectional diagrams of biaxial fiber batteries.

Traditional fiber batteries predominantly utilize carbon materials as current collectors and carriers for active materials (Hoshide et al., 2017; Huang et al., 2022; Huang et al., 2024; Lin et al., 2014; Luo et al., 2015; Rao et al., 2017; Ren et al., 2014; J. Wang et al., 2022; Wang et al., 2024). However, when fabricating large-scale, elongated batteries, they often encounter challenges such as high internal resistance [2]

and low tensile strength. To address these issues, researchers have successfully employed metal wires as current collectors in large-scale fiber batteries, effectively enhancing both internal resistance and tensile strength (He, Lu, Jiang, Han, Shi, Wu, Wang, Chen, Wang, Zhang, et al., 2021; Kwon et al., 2012; Liao et al., 2022; Lin et al., 2014; C. Lu et al., 2024; Park et al., 2015; Ren, Li, et al., 2013; Yu et al., 2013). This technique has now become widespread in the field of fiber batteries. Furthermore, advancements in extrusion processes, coupled with industrial production equipment, have enabled the mass production of kilometer-scale fiber battery products. These extrusion techniques involve the extrusion of a paste consisting of active materials, conductive materials, and binders (Liao et al., 2022). Additionally, similar extrusion process has been applied in laboratory settings to prevent the dendrites formation in aqueous zinc-ion fiber batteries (Pu et al., 2024). Common techniques involve the use of two fiber electrodes, either arranged parallelly (parallel biaxial fiber battery, PBFB) or intertwined (twisted biaxial fiber battery, TBFB), or one fiber electrode serving as the main axis with another wound around it to construct the fiber battery (Figure 3.1b) (Lin et al., 2014; Mo et al., 2020; Rao et al., 2017; Ren, Li, et al., 2013; Ren et al., 2014).

Compared to planar batteries, dual-fiber electrode batteries lack a fixed distance between the two electrode surfaces (Figure 3.1e) (Ren, Bai, et al., 2013; Tebyetekerwa et al., 2019; Zhang et al., 2014), making effective utilization of the active material challenging. In planar batteries, the consistent distance between cathode and anode surfaces facilitates the movement of active materials through the separator during charging and discharging (Figure 3.1d) (Li et al., 2015). However, in dual-fiber electrodes, the cylindrical surfaces result in limited contact area and increased distance between electrodes, leading to higher internal resistance. Additionally, regions where the electrodes are back-to-back further hinder active material participation, reducing the overall specific capacity. While stacking layers can address these issues in planar batteries, in fiber batteries exacerbate internal resistance and active material utilization challenges. Intertwining electrodes or wrapping one electrode around another can slightly increase contact length and area, but complete elimination of these issues remains elusive. Even with thicker cylindrical electrode as the main axis, the outer electrode's backside area still face difficulties in participating in the reaction, highlighting the unique challenges of intertwined dual-fiber batteries.

We have combined the conductive advantages of metal current collectors and the stable, compact design of planar battery electrodes into a uniaxial fiber battery (UAFB)(Figure 3.1a,1c). This innovative design combines a fiber electrode with a narrow strip electrode, significantly increasing the aspect ratio. The strip electrode utilizes a metal foil current collector, typically aluminium or copper for lithium-ion batteries and nickel for aqueous batteries or supercapacitors. One side of the metal foil is coated with a mixture of electrode material, then cut into narrow strips and tightly wound around the fiber electrode containing a separator. This arrangement maintains a consistent distance between the electrodes, akin to the separator thickness, and ensures both electrodes have a face-to-face structure for optimal utilization and specific capacity of the electrode material.

3.4 FIBER BATTERY WITH NEW STRUCTURAL DESIGN

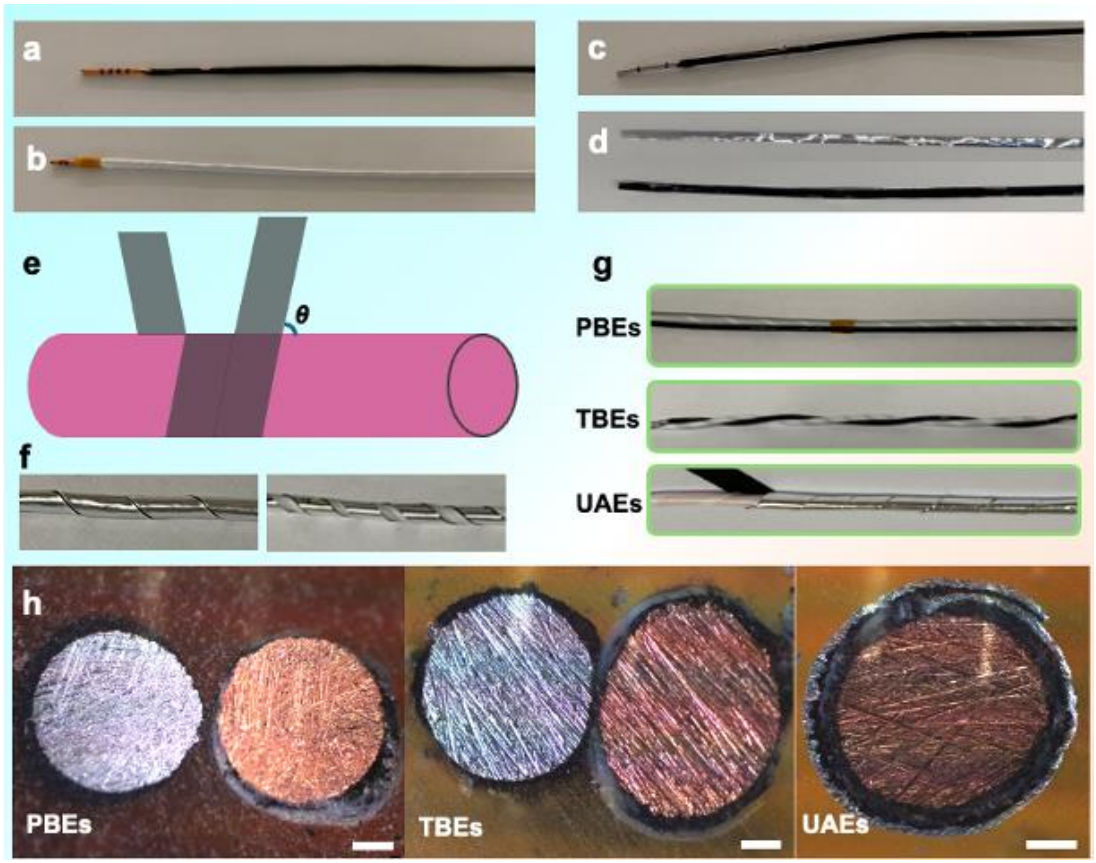
3.4.1 Biaxial fiber electrodes and uniaxial fiber electrodes

The fabrication process of Parallel Bifilar Electrodes (PBEs), Twisted Bifilar Electrodes (TBEs), and Uniaxial Electrodes (UAEs) is crucial for producing the three battery types, with electrode combinations distinguishing them. The electrodes may be encased in various outer shell; for instance, lithium-ion anodes and cathodes can be enclosed within aluminium plastic film, while aqueous electrodes can be within standard plastic shells. We scrutinized the differences in construction and performance among UAFs, TBFs, and PBFs to underscore the advantages of the novel uniaxial coaxial fiber battery. During fabrication, apart from the electrode manufacturing variances, all other conditions remain consistent. Metal wire serves as the current collector for all fiber electrodes, a critical element for fiber battery success. For the lithium-ion series, copper wire is used for anodes, and aluminum wire for cathodes. The fiber anode and cathode (Figure 3.2a, 2c) as well as the fiber anode wrapped with a separator (Figure 3.2b) maintain the typical fiber shape. Strip-shaped cathodes maintain the planar properties found in flat-plate cells, despite the extreme aspect ratio of this shape (Figure 3.2d). PBEs are two fiber electrodes placed in parallel. Due to the lack of restraint between the electrodes, they must be fixed with polyimide tape at intervals (Figure 3.2g, PBEs). Two fiber electrodes are entangled together in TBEs (Figure 3.2g, TBEs). The innovative structure of UAEs uses the strip-shaped ribbon cathode electrode wrapped around a separator-wrapped fiber anode (Figure 3.2g,

UAE). PBEs, TBEs, and UAEs all maintain the characteristics of fibers. These electrodes are packaged in a housing to form the corresponding battery (PBFB, TBFB, UAFB). See the Methods section for more detailed fabrication procedures.

Figure 3.2

Illustration of three methods of combining fiber electrodes.



Note. (a) The anode fiber electrode with electrode material applied to the copper wire. (b) The anode fiber electrode after the separator has been wound around it. (c) The cathode fiber electrode with electrode material coated on the aluminum wire. (d) The narrow strip-shaped cathode electrode after electrode material has been applied to one side of the aluminium foil and then cut. (e) A schematic showing the angles for winding the separator and the strip electrode. (f) The appearance of a UAEs at different winding angles: on the left, when the angle is set close to the perfect angle, there is slight overlap/gap on the outer electrode; on the right, when the angle is significantly less than the perfect angle, the gaps in the outer electrode increase. (g) The three electrode combinations from top to bottom: PBEs, TBEs, and UAEs. (h) Cross-sectional optical images of the three types of fiber electrode combinations, from left to right: PBEs,

TBFEs, UAEs. All scale bars are 200μm. Slight overlapping during the production of UAEs results in overlaps in some areas of the cross-sectional image; if there is a slight gap, the outer ring will have notches. Only when the winding is perfect does the outer side form a perfect circular ring.

In the fabrication of fiber batteries, wrapping the separator and the narrow strip electrode around the fiber electrode surface must be done at a specific angle, denoted as θ. This angle is defined as the angle between the direction of the fiber electrode and the direction of the separator/strip electrode. Reference angles for separator wrapping are provided in some advanced studies (Figure 3.2e), but due to variations in the radius of the fiber electrode (r) and the width of the separator (w), adjustments are necessary. We have theoretically derived a method for calculating this optimal wrapping angle based on the given r and w. To determine this angle, we mark the perfectly wrapped, non-overlapping, and gapless separator with horizontal lines, then unwind it for one complete revolution. The point on the right side of the penultimate revolution and the point on the left side of the last revolution align vertically after unwinding, forming a large right-angled triangle. In this triangle, one angle is θ, and the vertical line has a length equal to the fiber electrode's circumference, $2\pi r$. Next, we consider the length L of the horizontal line after unwinding. L and the separator width w form a smaller right-angled triangle, which also includes angle θ. With these two triangles, we can derive two equations:

$$\frac{2\times\pi\times r}{L} = \tan\theta \qquad (1)$$

$$\frac{w}{L} = \sin\theta \qquad (2)$$

Based on these two equations, we can deduce the formula to calculate angle θ:

$$\theta = cos^{-1}\left(\frac{w}{2\times\pi\times r}\right) \qquad (3)$$

From equation 3, it can be derived that as the width w approaches zero, the wrapping angle approaches 90 degrees, and as w approaches the circumference of the fiber electrode, the overwrap angle tends towards zero degrees. The width of the separator cannot be arbitrary; for θ to be meaningful and achieve perfect wrapping, the width w of the separator must be less than the circumference of the fiber electrode. Based on this, the wrapping angle is calculated using equation 3. When the wrapping

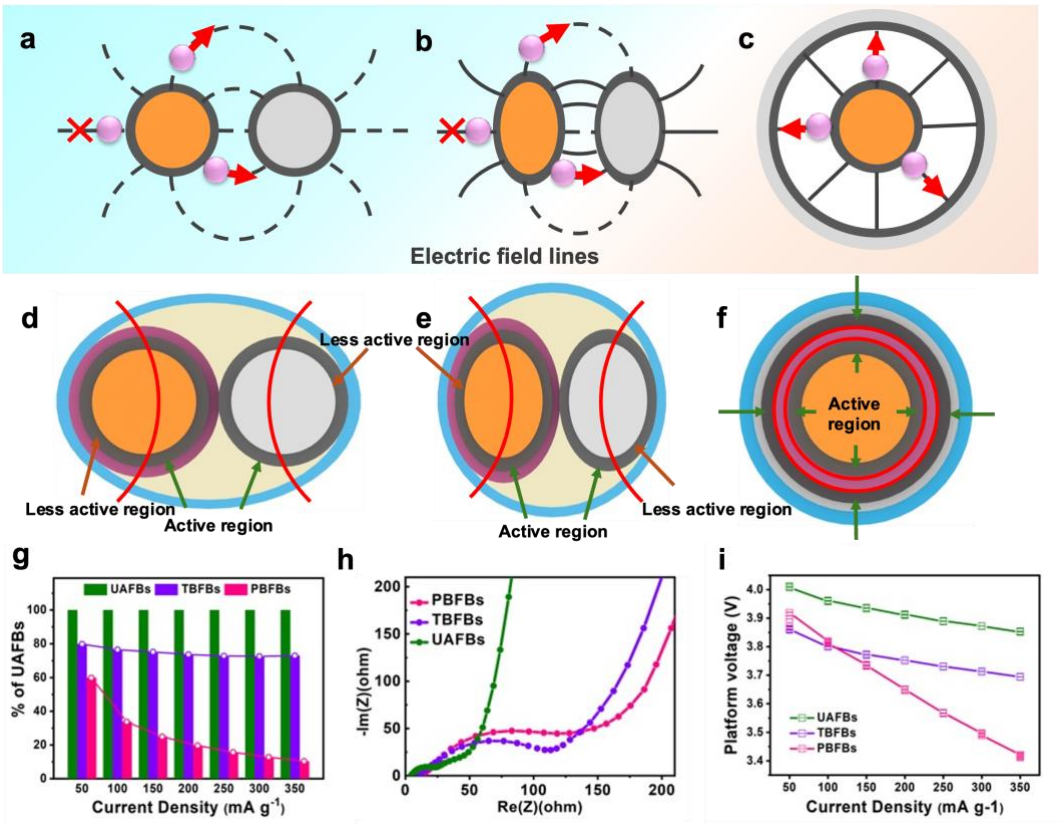
angle is greater than θ, overlapping of the wrap will occur; when the wrapping angle is less than θ, gaps will appear. With this knowledge, we can adopt appropriate strategies when manufacturing fiber batteries. When wrapping the separator, there must be no gaps to prevent internal short-circuiting of the battery, hence the wrapping angle should be slightly greater than θ to ensure that all fiber electrodes are covered by the separator. In the fabrication of UAEs, the wrapping angle is set around θ, allowing for a minimal gap or overlap in the external wrapping electrode (see the left side of Figure 3.2f). Excessive gaps will reduce the face-to-face contact area between the outer electrode and the fiber electrode, resulting in parts of the fiber electrode uncovered by the outer electrode (see the right side of Figure 3.2f). This knowledge enables appropriate strategies for manufacturing fiber batteries to ensure reliable performance and optimal coverage.

We compared the cross-sectional images of PBEs, TBFEs, and UAEs (Figure 3.2h) to visually demonstrate their combined advantages of planar batteries while maintaining a fiber shape, focusing on internal resistance and material utilization efficiency. In PBEs, the distance between the two circular electrode surfaces ranges from the separator thickness d to the sum of the radii of the two fiber electrodes $r_{\text{cathode}} + r_{\text{anode}}$. However, due to the lack of constraint between the electrodes , this distance is often greater than d, including any gaps present. For TBEs, the intertwined design results in a double-ellipse cross-section, reducing the distance between electrodes compared to PBEs and ensuring closer contact, with the minimum distance typically being the separator thickness. The more tightly the electrodes are wound, the more this effect is enhanced. UAEs maintain a constant distance equal to the separator thickness , with the outer electrode coated only on the inner side, ensuring a face-to-face contact between electrode materials. The outer side of the outer electrode acts as a current collector, unlike methods that directly coat electrode material on the fiber electrode side with the separator. This design, featuring a metal foil current collector layer, ensures low ohmic resistance in long fiber batteries. An alternative method involves applying electrode slurry with carbon nanotubes directly to the fiber electrode with the separator. However, this method is significantly more costly due to the high amount of carbon nanotubes needed to ensure low internal resistance compared to the metal foil strip electrode.

3.4.2 Biaxial fiber batteries and uniaxial fiber batteries

Figure 3.3

Comparative analysis of discharge capabilities and contributing factors among three types of fiber batteries.



Note. (a), (b), and (c) Schematic representations of electric field lines during discharge for Parallel Bifilar Fiber Batteries (PBFBs), Twisted Bifilar Fiber Batteries (TBFBs), and Uniaxial Coaxial Fiber Batteries (UAFBs), respectively. (d), (e), and (f) Illustrations of active regions (green arrow) and less active regions (red arrow) within PBFBs, TBFBs, and UAFBs. (g) Discharge capabilities comparison at different current densities, with UAFBs' discharge capacity at each current density serving as the baseline (100%). (h) Electrochemical impedance spectroscopy of three fiber batteries. (i) Comparison of discharge plateau voltages of the three fiber batteries across varying current densities.

In batteries, reaction ions tend to move along the electric field lines. When the battery is fully charged and in an open-circuit state, the anode surface is rich in lithium cations, whereas the cathode surface is densely packed with anions. Upon activation,

electrons move along the external circuit to the cathode, rendering the anode positively charged and the cathode negatively charged; with electric field lines forming between them as shown in Figure 3.3a-3c. In the face-to-face and top-bottom areas, lithium ions are attracted to the cathode by the electric field, where they undergo an electrochemical reaction, designing these regions as electrochemically active. In dual-axial fiber batteries, the back-to-back parts have a long path for the electric field lines, hindering lithium ion movement from the anode to the cathode, thus hindering the anode oxidation reaction. At the same time, the reduction reaction on the back of the cathode is hindered due to the lack of lithium ions, making these non-active area (Figure 3.3d, 3e). Consequently, the active material in these regions does not participate in the discharge process, reducing the specific capacity of the active material. In coaxial fiber batteries, the electric field lines radiate from the central fiber (Figure 3.3c, 3f), ensuring that all materials in all areas participate in the reaction, thereby maximizing the utilization rate and specific capacity of the active material.

To verify this hypothesis, we conducted tests on three types of fiber lithium-ion batteries, using commercial lithium cobalt oxide and synthetic graphite as electrode active materials, PVDF as a binder, and super-P as a conductive agent, along with a commercial lithium-ion electrolyte. Ensuring an excess of cathode to facilitate the formation of an SEI layer and adequate lithium intercalation, we maintained consistency across all materials used in the three battery types. Consequently, the anode specific capacity was solely affected by the form factor of battery. Discharge at a current density of 50 mA g^{-1}, the charge-discharge curves and specific capacity data as shown in Figure 3g reveal specific capacities of 267.9 mAh g^{-1} for UAFBs, 213.9 mAh g^{-1} for TBFBs, and 160.3 mAh g^{-1} for PBFBs, respectively, based on the mass of anode active material. While we focus on assessing the impact of the new battery design, material data is not the primary focus here. Considering the specific capacity of the coaxial fiber battery under varying current densities as 100% (Figure 3g, Table 3), TBFBs demonstrated specific capacity is 79.8% at 50 mA g^{-1}, indicating 79.8% active area. Unlike UAFBs where all areas are active, TBFBs exhibited over half of the arc surface area active, including face-to-face, top, and bottom area, with the non-active area at the back constituting about 20.2% of the total arc surface. PBFBs displayed a specific capacity of 59.8%, exceeding 50% and covering more than half of the total arc surface area, for similar reasons as TBFBs, albeit to a lesser extent.

TBFBs, featuring a double elliptical cross-section compared to PBFBs' double circular cross-section, showcased closer contact in the face-to-face area, thereby better demonstrating the specific capacity of the active material. As current density increased, TBFBs and PBFBs showed a gradual decline in percentage relative to UAFBs at the same current density, highlighting the structural advantages of UAEs under high currents, with the advantage increasing as the current density amplifying as the current density rose. Electrochemical impedance spectroscopy (Figure 3.3h) can well explain the reason. Due to their structural advantages, UAFBs have the smallest radius in the EIS, revealing their lowest charge transfer resistance. At the same time, UAFBs have the steepest slope, close to 90 degrees, which is very similar to the characteristics of flat capacitors, revealing that UAFBs inherit the advantages of flat batteries. The slopes of TBFBs and PBFBs decrease, indicating that the ion diffusion process between the two electrodes is partly similar to spherical diffusion, which is consistent with the structure of the double arc electrode. The battery's discharge voltage platform (Figure 3.3i) shows a higher voltage platform of UAFBs, indicating their lower battery internal resistance. UAFBs show a high plateau voltage under various discharge currents, and as the discharge current increases, the plateau voltage decreases minimally. The platform voltage of PBFBs is close to that of TBFBs at low current. As the discharge current increases, the platform voltage decreases rapidly, thereby reducing its discharge capacity. Both EIS and voltage plateau show that the structural design of UAFBs can greatly improve the rate discharge capability of fiber batteries.

The arc-shaped cross-section not only impacts the active area due to the varying distances that ions must travel between electrodes, but it also theoretically affects the internal resistance of battery. We demonstrate this by modelling the internal resistance caused by ion movement for a standard double-circular cross-section and a ring-shaped cross-section. In the dual-fiber battery, the cross-section is standard double-circular with the closest distance between the two electrodes being the separator thickness d, and both cylindrical electrodes having a uniform radius r and length L (approximating the length of the fiber battery). The space between the two electrodes is infinitely divided into rectangular channels, starting from the line connecting the centers of the two circular electrodes, extending upwards and downwards to the bottom and top of the circle, symmetrically. Assuming the upper half of the cross-section is evenly divided into $\frac{r}{h}$ segments, each with a height h, in the x-th segment where ($x =$

$1,\ 2,\ 3 \ldots \frac{r}{h})$, the area for ion movement is hL, and the ion travel distance is $\mathrm{d} + 2r - 2\sqrt{r^2 - (xh)^2}$. This distance, $r - \sqrt{r^2 - (xh)^2}$, is calculated using the radius and Pythagorean theorem. Assuming the electrolyte conductivity is κ (typically a constant value for a given electrolyte), the conductivity of this area is given by Equation 4. Since the ion resistance is the inverse of conductivity and the rectangles are in parallel, they are considered a series of parallel resistances, with the bottom resistances equal to the top ones. The total resistance can be expressed as Equation 5:

$$\lim_{h \to 0} f(x) = \frac{\kappa h L}{\mathrm{d} + 2r - 2\sqrt{r^2 - (xh)^2}} \qquad (4)$$

$$R_E = \frac{1}{2 \times (\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \cdots + \frac{1}{R_n})} = \lim_{h \to 0} \frac{\mathbf{1}}{\mathbf{2} \times (\sum_{\mathbf{1}}^{r/h} \boldsymbol{f(x)})} \qquad (5)$$

Where $k, L, d,\ r$ are constants, h approaches zero, and x is an integer from 1 to $\frac{r}{h}$.

For the UAEs, the cross-section is a ring, where the distance between the two electrodes remains fixed at the separator thickness d. With the same electrolyte conductivity κ, the ion passage area is A. The conductance is calculated as $= \kappa \frac{A}{d} = \frac{1}{R}$, which is the inverse of the resistance R. The area A can be determined by unrolling the cylindrical surface along the fiber direction into a rectangle. This large area A has a width equal to the circumference of the cross-section, $2\pi r$, and length equal to the length of the fiber electrode/battery L. The ion movement resistance can be expressed as Equation 6:

$$R_E = \frac{d}{\kappa A} = \frac{d}{\kappa 2\pi r L} \quad (6)$$

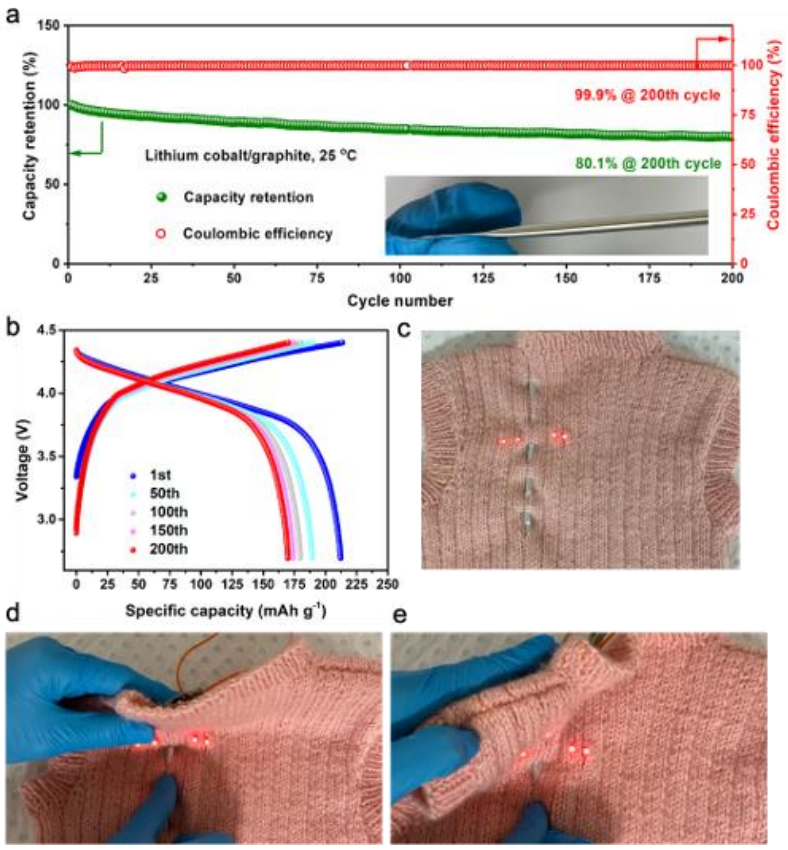
3.4.3 Practicality of uniaxial fiber batteries

Finally, we simulated the cycling characteristics of the uniaxial fiber battery during practical use. The initial cycle capacity was set to 100%, and after 200 cycles, the battery still maintained over 80% of its capacity (Figure 3.4a). The charge-discharge curves showed no significant distortion throughout the cycles (Figure 3.4b), and the Coulombic efficiency remained stable, close to 100%. In wearable and other electronic devices, a remaining capacity of 80% is often used as a criterion for the end of battery life. Applied to wearable electronic devices, this type of fiber battery can

guarantee a lifespan of 200 cycles, demonstrating practical application value. At present, the capacity of the most advanced liquid electrolyte fiber battery [1,14,15] rapidly decays within 100 cycles. In contrast, the innovative structural design of this study greatly makes up for the shortcomings of the fiber battery in terms of cycle performance. We wove this fiber battery into clothing, successfully lighting up the LED array in the clothing, and maintaining illumination function during bending and twisting (Figure 3.4c, Video S1, Video S2). The capacity, cycle life, flexibility and the wearable nature of the UAFBs already meet the power supply requirements of a variety of devices, such as wearable screens, wearable detection equipment, and wearable smart devices. It can also be transformed into a cloth battery to power various mobile devices, such as outdoor camping equipment and outdoor lighting. This new structure of fiber battery will have a wide range of application scenarios and market potential.

Figure 3.4

Cycling capability of UAFBs.



Note. (a) Capacity retention of UAFBs over 200 cycles, the inner photograph illustrates the assembled UAFBs. (b) The specific capacity-voltage curves during

charging and discharging throughout the cycling process of UAFBs. (c) Demonstration of UAFBs products powering LED arrays. The fiber battery can normally power LED lights when bent (d) and twisted (e).

3.5 CONCLUSION

By integrating the structure of planar batteries with the form of fiber batteries, our designed uniaxial fiber batteries (UAFBs) achieved higher discharge capability than traditional bifilar fiber batteries. Its unique cross-sectional construction maintains a constant distance between the anode and cathode, and the face-to-face design ensure all areas of the electrodes are active, significantly reducing the internal resistance. The results demonstrated that UAFBs, using commercial lithium cobalt oxide and synthetic graphite as electrode materials, maintain over 80% of their capacity after 200 cycles, meeting the practical application criteria for wearable electronics. This innovative design not only enhances material utilization and internal resistance but also offers a sustainable and cost-effective solution by potentially incorporating recycled silicon from discarded photovoltaic panels. This approach addresses both resource utilization and environmental protection challenges, highlighting the UAFBs' practical application value in the field of wearable electronics.

3.6 MATERIALS AND METHODS

3.6.1 Preparation of electrode slurry

Commercial lithium cobalt oxide is used as the cathode active material, commercial synthetic graphite as the anode active material, Super-P as the conductive material, PVDF as the binder, and NMP as the solvent. A solid powder mixture is prepared with a mass ratio of active material: conductive material: binder = 8:1:1. To make the slurry, mix 1g of the solid material with 3mL of solvent and stir until well combined.

3.6.2 Preparation of fiber electrodes

Copper wire is paired with anode slurry, and aluminium wire with cathode slurry. Before use, copper and aluminium wires are wiped with a cloth soaked in ethanol. Each wire is dipped into the electrode slurry, then slowly withdrawn, and instantly

dried using a hot air blower. Then, they are dried in a vacuum oven at 70°C for 24 hours. The dried fiber electrodes are cut to a specific length for use.

3.6.3 Preparation of fiber batteries

The separator is cut into narrow strips and wound around the fiber anode at a calculated angle to create the separator-wrapped fiber anode. For PBFBs (Parallel Bifilar Fiber Batteries), the fiber cathode and the separator-wrapped fiber anode are arranged parallelly, placed into an aluminium-plastic film casing, filled with commercial lithium-ion electrolyte, and sealed. For TBFBs (Twisted Bifilar Fiber Batteries), the fiber cathode and separator-wrapped fiber anode are twisted together, placed into an aluminium-plastic film casing, filled with commercial lithium-ion electrolyte, and sealed. For UAFBs (Uniaxial Fiber Batteries), the strip-shaped cathode with electrode material on one side is positioned facing the separator-wrapped fiber anode, wound at the calculated angle, placed into an aluminium-plastic film casing, filled with commercial lithium-ion electrolyte, and seale

Chapter 4: Conclusion and Outlook

4.1 CONCLUSION

In summary, this thesis discusses in depth the realization of flexible batteries, and carries out two research works from two perspectives: the preparation of flexible electrode materials and flexible electrodes and their final application in lithium-ion batteries and sodium-ion batteries, and the structure of the new fiber battery that combines the advantages of flat batteries, relying on the flexibility and low latitude of fiber batteries to achieve higher-dimensional flexible battery preparation.

In Chapter 1, a detailed literature study on flexible batteries was conducted, including research on the flexibility of one-dimensional and two-dimensional flexible energy storage devices in terms of stretching, twisting, and bending, as well as research on how to achieve overall flexibility from the perspective of battery structure. This chapter summarizes the existing research progress of flexible energy storage devices, and looks forward to how to further improve the flexibility and electrochemical performance of flexible batteries from the perspective of battery structure, electrodes, electrolytes/separators, and packaging materials. In addition, the characteristics of organic materials are reviewed, providing a literature basis for the subsequent application of organic materials in flexible batteries.

The inspiration for the work in Chapter 2 comes from daily life. Books inherit the flexibility of a single sheet of paper, and can be bent while maintaining a relatively thick thickness. This property is used to make flexible electrodes and obtain good surface capacity. It is also used in lithium-ion batteries and sodium-ion batteries, and flexible batteries are used in wearable devices such as smart watches and smart insoles.

The work in Chapter 3 combines the advantages of the most advanced fiber battery morphology and the electrochemical performance of planar batteries to invent a new type of battery structure - coaxial fiber battery. This battery has excellent electrochemical performance and maintains the shape and flexibility of fiber batteries.

This thesis advances the development of flexible batteries by exploring both material and structural innovations. It focuses on flexible electrode materials, flexible electrodes, and their application in lithium-ion and sodium-ion batteries, as well as the

creation of a coaxial fiber battery. The research enhances the understanding of flexibility in energy storage devices, offering insights for future applications in wearable technologies and next-generation energy solutions.

4.2 OUTLOOK

As described in this paper, with the development of smart wearable devices and their broad potential applications, flexible batteries will have broad demand and application prospects in the future. According to the characteristics and needs of flexible batteries, the flexibility of batteries can be achieved from various aspects:

New materials. Materials are the basis of batteries, and the realization of flexible batteries requires the combination of materials with different characteristics. Finding materials that are more suitable for flexible batteries will be one of the focuses of future flexible battery research. Such materials need to be flexible in the macroscopic sense and have the characteristics of their applications in terms of function, for example: electrode materials also need to be electrochemically active, diaphragm materials or electrolytes need to have ionic conductivity, and shell materials need to seal the inside and outside of the battery to isolate air and water.

New structure. Based on the materials, various materials are used to design different structures to achieve flexibility. Even some materials that do not have macroscopic flexibility can also achieve overall battery flexibility by using sophisticated structural innovations. In addition to book-shaped flexible electrodes, accordion-shaped flexible electrode designs, and spine-shaped flexible battery designs, I believe there will be other better ways to achieve flexible electrodes. Using existing commercial materials combined with innovative structural designs may be one of the ways to quickly commercialize flexible batteries.

Bottom-up flexible implementation method. How to prepare low-dimensional flexible batteries by combining them into large high-dimensional flexible batteries will become another research hotspot. Usually one-dimensional batteries or fiber batteries are naturally flexible. Such low-dimensional batteries can be assembled into higher-dimensional batteries, making the high-dimensional batteries flexible. Large-scale preparation of fiber batteries with excellent electrochemical properties and finding out how to weave such batteries into cloth on a large scale will become a potential way to realize flexible batteries in the future.

Appendices

Appendix A

Tables

Table 1

Cost per watt-hour comparison of three cathode materials

Materials	Battery systems	Costs of cathode materials per Wh (CNY)
P-chloranil	P-chloranil-Pb	0.05
PbO_2 (based on raw material lead ingot)	PbO_2-Pb	0.06
$LiCoO_2$	$LiCoO_2$-graphite	0.22

Table 2

A summary of electrode, electrolyte/diaphragm, packaging materials, flexible type and bending performance of typical flexible batteries/supercapacitors

	Type of device	Flexible type	Performance	Electrode materials	Electrolyte/ diaphragm materials	Packaging materials	Ref.
1D	Supercapacitor	Stretched, bent	Maximum 370%	CNT	PVA/H3PO4/water hydrogel	None	(Chen et al., 2015)
	Hybrid of lithium-ion battery and supercapacitor	Bent	>180°	CNT, carbon, Li4Ti5O12, LiMn2O4	LiTFSI/SCN/PEO gel electrolyte	None	(Zhang et al., 2015)
2D	Li-ion battery	Stretchable, bent	Maximum 22% stretching, 180° bent	LCO, graphite, metal foil	LiPF6 in ethylene carbonate/diethyl carbonate, Celgard separators	Aluminized pouch bags	(Shi et al., 2019)
	Li-ion battery	Stretchable	Maximum 400%	LTO, LMO, CNT, elastic substrate	LiTFSI/SCN/PEO gel electrolyte	PDMS film	(Weng et al., 2015)
	Li-ion battery	Stretchable	Maximum 300%	LiMn2O4, V2O5, silver coated elastic substrate	Polyacrylamide/water-in-salt hydrogel electrolyte	PDMS film, epoxy glue	(X. Chen et al., 2019)
	Li-ion battery	Bent	180°	PDI, TPU, carbon cloth	LiPF6 in ethylene carbonate/diethyl carbonate, Celgard separators	Aluminized pouch bags	(Lie Ma et al., 2019)
	Supercapacitor	Bent	180°	Graphene, V_2O_5	LiPF6 in ethylene carbonate/diethyl carbonate, Celgard separators	Aluminized pouch bags	(Haiqing Liu et al., 2017)
	Li-ion battery & Na-ion battery	Bent	180°	CNT, PTCDI	Commercial electrolyte	Aluminized pouch bags	(Huang et al., 2022)
	Li-ion battery	Bent, twisted	About 180° bent, about 60° twist	LiCoO2, graphite, metal foil	LiPF6 in ethylene carbonate/diethyl carbonate, Celgard separators	Aluminized pouch bags	(Qian et al., 2018)

Table 3

The areal capacity of the book-like electrode in flexible LIB & SIB is compared with other work.

Published date	Current density (mA g^{-1})	Areal capacity (mAh cm^{-2})	Materials	Flexible Batteries	Journal	Ref.
2022/2/6	83.75	5.2	O-Ti_3C_2@CNF	LIB	*Energy Stor. Mater.*	(He et al., 2022)
2021/3/3	17	4.56	LFP/CNT/EVA	LIB	*Adv. Funct. Mater*	(Zhang et al., 2021)
2020/4/1	98	4.78	P@MOF/CNT/CFC	LIB	*Chem. Eng. J.*	(Wu et al., 2020)
2019/11/4	28.2	2.01	$LiMn_2O_4$@GCN	LIB	*Nano Energy*	(Yu et al., 2020)
2017/7/31	100	0.56	V2O5@polydopamine@carbon cloth	LIB	*J. Power Sources*	(Ma et al., 2017)
2017/2/27	138	1.4	N-doped carbon@$LiTi_2(PO_4)_3$	LIB	*J. Mater. Chem. A*	(Weng et al., 2017)
2016/2/10	37.2	0.25	3D CNTs	LIB	*Nanotechnoloy*	(C. W. Kang et al., 2016)
2021/8/24	20	4.5	TiO_2-C	SIB	*Infomat*	(H. W. Wang et al., 2022)
2020/5/20	40	2.45	3D porous graphene nanosheet/SnS_2	SIB	*Small*	(Sang et al., 2020)
2019/11/26	32	0.76	$K_2Zn_3(Fe(CN)_6)_2 \cdot 9H_2O$@carbon cloth	SIB	*Small*	(He et al., 2019)
2019/1/7	83	2.12	3D Carbon-Networks/Fe_7S_8/Graphene	SIB	*Adv. Mater.*	(W. H. Chen et al., 2019)
This work	100	5.88	Book-like PTCDA@CNTs	LIB	*ChemComm*	(Huang et al., 2022)
	27.32	5.24		SIB		

Appendix B

Publications list

Huang, T., Long, M., Xiao, J., Liu, H., & Wang, G. (2021). Recent research on emerging organic electrode materials for energy storage. *Energy Materials*, 1(1):100009. https://doi.org/10.20517/energymater.2021.09

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Appendix C

Conference attended during the doctoral candidature

4th International Conference on Emerging Advanced Nanomaterials ICEAN 2022. (17/10/2022~21/10/2022)

Oral presentation: “A thick, Flexible Book-like Electrode for Lithium-ion Batteries and Sodium-ion Batteries”. (On behalf of Distinguished Professor Guoxiu Wang)

Appendix D

Awards during the doctoral candidature

Paper of the Month August-September 2024, University of Technology Sydney.

(10/2022)

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