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**ENERGY-DENSE FLEXIBLE LI-
ION BATTERIES BASED ON
ULTRALIGHT METAL-COATED
FABRICS**

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Ph.D

The Hong Kong Polytechnic University

2024

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**Energy-dense Flexible Li-ion
Batteries based on Ultralight
Metal-coated Fabrics**

YU Wancheng

**A thesis submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy**

August 2023

CERTIFICATE OF ORIGINALITY

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ABSTRACT

Li-ion batteries (LIBs) are the most essential energy storage devices in daily life because of their advantages of high energy density, no memory effect and mature production techniques. Besides increasing energy density, rendering the LIBs with high flexibility has become another critical research topic to power flexible or wearable electronics. Hundreds of works have been proposed to realize flexible lithium batteries (FLBs), and these methods can be simply classified into two major strategies: soft structure and soft materials. Structure design can protect the rigid parts of LIBs by controlling the distribution of stress, however, getting flexibility usually leads to lower energy density because of the introduction of inactive components or inferior electrochemical performance. Although using carbonaceous materials such as carbon nanotubes (CNTs) and graphene as current collectors can essentially improve the deformability of the battery, their preparations are complex and expensive. Hence, it is necessary to develop new kinds of current collectors that manifest comprehensive properties combined with low cost, low areal density, high conductivity, excellent flexibility, and outstanding electrochemical stability, to manufacture highly flexible and energy-dense FLBs.

First, the polymer-assisted metal deposition (PAMD) method is adopted for wrapping metal layers (Cu and Ni) on thin glass-fiber fabrics (GFs). GFs are widely used as insulating material because of their high strength, deformability, and chemical stability. The polymer interlayer facilitates a more stable interfacial adhesion between the metal layer and GFs. As a result, metal-coated GFs (MGFs) exhibit qualified electrical conductivity and excellent mechanical durability. With much lower areal densities (2.9-

3.2 mg cm⁻²) than Cu foil (7.5 mg cm⁻²) and Al foil (4.2 mg cm⁻²), the FLBs using MGFs show improvements of 9~18% on the energy density. In addition, the MGF-based pouch cell shows a high capacity retention of 94.1% after 500 bending cycles at radius of 5 mm and another 500 bending cycles at 2 mm.

Then, a flexible and high-voltage current collector was fabricated by the modified electroless deposition (ELD) method. It was found that the working potential range of Ni-coated GF (NiGF) is just up to 4 V vs. Li/Li⁺, which can only support the lithium iron phosphate (LFP), a low-energy cathode material. Hence, Ni coating is replaced with the Ni/P composite to increase the anodic stability of the cathode current collector. The resultant Ni/P composite-coated GF (NiPGF) is proved to be a qualified high-voltage current collector with an onset anodic potential of ~4.7 V. Also, NiPGF-based electrodes display similar electrochemical performances to Al-based electrodes with lower areal density and much better flexibility. The atomic layer deposition (ALD) method protects the P from dissolution, resulting in a reasonable cyclic performance for the full cell using NiPGF. Dynamic bending test indicates the stable power output of the NiPGF-based pouch cell under a low bending radius of 5 mm.

At last, the polymer fabrics substrate with lower areal density and better mechanical properties is applied to further increase the energy density and flexibility of the FLB. Unlike glass fiber, polyethylene terephthalate (PET) is soft in nature, which makes the resultant fabrics more resilient. However, PET is not as inertial as GFs so the side reactions become an urgent issue to be addressed. The degradation mechanism is clarified by the careful characterizations of the Fourier transform infrared spectroscopy (FTIR) and the morphology change of Cu-coated PET fabrics (CuPET) during the ELD

process. After the additional electroplating of Cu, the PET substrate is fully covered and separated from the electrolyte. A high energy density of 207 Wh kg^{-1} is achieved for the full cell using metal-coated PET fabrics (MPETs), which is 17% higher than that of the full cell using metal foils. By inheriting the excellent mechanical flexibility of PET fabrics, the pouch cell shows high capacity retention of $\sim 80\%$ after the bending test that 500 bending cycles for each bending radius (5 mm, 2mm and 1 mm) was conducted. In a rigorous and continuous bending process of 3 mm, the pouch cell maintains $\sim 87\%$ discharging capacity compared to the flat state.

In summary, we propose a series of flexible, superlight, highly conductive, and electrochemically stable fabric-based current collectors. Compared to commercially used Cu and Al foils, they display much lower areal density and better deformability. It means that we can improve the energy density and flexibility of the FLB, simultaneously, by using fabric-based current collectors. The transplantable preparation and protection methods in this thesis pave the way for manufacturing textile-based current collectors for future large production of FLBs.

LIST OF PUBLICATIONS

Published papers:

1. Jian Shang,[#] **Wancheng Yu**,[#] Lei Wang,[#] Chuan Xie, Hailong Xu, Wenshuo Wang, Qiyao Huang, Zijian Zheng*, Metallic Glass Fiber Fabrics: A New Type of Flexible, Super-Lightweight, and Three-Dimensional Current Collectors for Lithium Batteries. *Adv. Mater.* **2023**, 2211748.
2. Jiehua Cai, Lei Wang, Qiyao Huang, **Wancheng Yu**, Chuan Xie, Zijian Zheng*, A Thin, Stable, and Flexible Janus Lithium-Textile Anode for Long-Life and High-Energy Lithium Metal Battery. *Adv. Energy Mater.* **2023**, 2303088.

Papers in preparation

1. **Wancheng Yu**, Lei Wang, Jian Shang, Hailong Xu, Zhenyao Wei, Yufeng Luo, Jiehua Cai, Chuan Xie, Yanpeng Guo, Zijian Zheng*, Ultralight Polyethylene Terephthalate (PET) Fabric-based Composite Current Collector for Energy-dense Flexible Li-ion Batteries.
2. **Wancheng Yu**, Yufeng Luo, Zhenyao Wei, Jiehua Cai, Zijian Zheng*, High-Voltage Textile-based Current Collector for High-energy Li-ion batteries.

Patent in investigation

1. Zijian Zheng, **Wancheng Yu**, Yufeng Luo,, High-voltage and flexible fabric current collector based on the Ni/P composite.
2. Zijian Zheng, **Wancheng Yu**. Flexible, lightweight, and electrochemically stable polyethylene terephthalate (PET) fabrics for anode current collector

ACKNOWLEDGEMENTS

This project is in process under the supervision of Prof. Zijian Zheng. Firstly, I want to extend my most sincere thank to my supervisor for his instructive guidance and advice. He taught us how to become an excellent researcher: think more, question more and do more. What is most impressive to me is that he repeatedly told us to query the published works and think independently no matter what story they told or what mechanism they proposed. Science is noble.

I also give my thank to all the current and former members in Dr. Zheng's group from whom I've gained kind support in both research and daily life (Dr. Yufeng Luo, Dr. Lei Wang, Dr. Jian Shang, Dr. Hailong Xu, Dr. Yaokang Zhang, Dr. Sze Wing, Miya, Ng, Dr. Hong Hu, Dr. Wenjiao Ge, Dr. Qiyao Huang, Dr. Yi Pei, Dr. Yuan Gao, Dr. Chuan Xie, Dr. Pengwei Wang, Dr. Yanpeng Guo, Dr. Haining Fan, Dr. Yingsi Wu, Dr. Ziran Wang, Dr. Yichun Ding, Dr. Yuqi Zhang, Dr. Wenshuo Wang, Dr. Junling Xu, Dr. Puifai Ng, Dr. Chi Zhang, Dr. Junhua Zhou, Dr. Huimin Wang, Dr. Jingjing Fu, Dr. Yufei Zhang, Dr. Chao Wang, Dr. Shuaichen Wang, Dr. Qianyi Guo, Dr. Mingming Rong, Ms. Qiuna Zhuang, Ms. Leni Zhong, Ms. Jiehua Cai, Ms. Yuqing Shi, Mr. Zhenyao Wei, Mr. Zijian Chen, Mr. Fan Chen, Mr. Pengxiang Zhang, Mr. Lingtao Fang, Mr. Xiaohao Ma, Ms. Shujing Wen, Mr. Lixi Chen, Mr. Jinxing Jiang, Ms Wudi Li).

At last, I would like to express my sincere gratitude to my parents and girlfriend. Thanks for your encouragement, support and understanding.

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LIST OF ABBREVIATIONS

LIBs	Li-ion batteries
LMBs	Li-metal batteries
FLBs	Flexible lithium batteries
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
CNTs	Carbon nanotubes
CNF	Carbon nanofiber
GO	Graphene oxide
rGO	Reduced graphene oxide
LFP	Lithium iron phosphate
LCO	Lithium cobalt oxide
NCM	Lithium nickel cobalt manganese oxides
NCA	Lithium nickel cobalt aluminum oxides
LCP	Lithium cobalt phosphate
LTS	Lithium titanium sulfide
Gr	Graphite
PE	polyethylene
PP	polypropylene
PET	polyethylene terephthalate
PI	polyimide
PPy	polypyrrole
PVDF	polyvinylidene fluoride

MPTS	3-(trimethoxysilyl)propyl methacrylate
METAC	[2-methacryloyloxy)ethyl]trimethylammonium chloride
DMAB	Borane-dimethylamine complex
KPS	potassium persulfate
NMP	1-Methyl-2-pyrrolidinone
GF	Glass-fiber fabric
MGF	Metal-coated glass-fiber fabric
MPET	Metal-coated polyethylene terephthalate fabric
CuGF	Cu-coated glass-fiber fabric
NiGF	Ni-coated glass-fiber fabric
NiPGF	Ni/P composite-coated glass-fiber fabric
CuPET	Cu-coated polyethylene terephthalate fabric
ECuPET	Cu-coated polyethylene terephthalate fabric with electroplated Cu
NiPPET	Ni/P composite-coated polyethylene terephthalate fabric
SEI	Solid electrolyte interface
CE	Coulombic efficiency
PAMD	Polymer-assisted metal deposition
ELD	Electroless deposition
ALD	Atomic layer deposition
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field-emission scanning electron microscopy
XRD	X-ray diffraction
FTIR	Fourier-transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy

LSV	Linear scanning voltammetry
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
GCD	Galvanostatic charge-discharge

Chapter 1. Introduction

1.1 Background and Challenge

Flexible or wearable electronics have become a research hotspot due to their potential applications in different areas such as communication,^{1, 2} healthcare,^{3, 4} and sensors.⁵⁻⁹ Energy storage devices are indispensable components in these advanced systems as they are the power sources to support the normal functions of electronics. By virtue of high energy density, no memory effect, and mature production technology, Lithium batteries are a promising candidate to fulfill the requirement of future electronics.¹⁰⁻¹² However, conventional Lithium batteries show little flexibility due to a rigid structure and low deformability of battery components.^{13, 14}

Traditional Li-ion batteries (LIBs) consist of four main components: the current collector, the active material composite layer, the separator, and the electrolyte. Separators are usually made of polyethylene (PE) and polypropylene (PP) which have enough deformation ability. The liquid electrolyte in the system almost has no influence on the flexibility of the battery. The vulnerable parts are the current collector and active material composite layer. Cu foil and Al foil are the best choices of current collectors for the anode and the cathode, in consideration of the cost, electrochemical stability, mechanical performance, and electrical conductivity. However, metal foils are not qualified as flexible current collectors due to their rigid and fatigability nature, making them unreliable in repeated deformation. Besides the current collectors, the active material composite layer is not flexible, especially when the mass loading is high. Although binders and porosity in the active material composite can buffer the

mechanical strain to some extent, it is easy to crack in a large deformation or delaminated from the current collector.¹⁵

Much effort has been made for improving the flexibility of LIBs.¹⁶ Two major strategies, namely “soft material” and “soft structure” were widely adopted.¹⁷ For the soft material strategy, metal foil-based current collectors were replaced by other materials, among which carbon-based nanomaterials such as carbon nanotube (CNT) film or graphene film are highly promising due to their excellent flexibility, conductivity, and electrochemical stability.^{18, 19} On the other hand, the structure of traditional batteries was partially or totally changed to endow the whole system with certain deformation ability, namely soft structure. Generally, rigid components are protected by the “sacrificial part” with a large breaking strain. It means that the applied stress and strain are not evenly distributed in the system, but the rigid part only withstands a small fraction of stress.

However, getting flexible inevitably sacrifices the energy density or specific energy due to the introduction of non-active materials. It is more typical for batteries using a soft structure strategy, in which the specific energy (or energy density) largely depends on the ratio between rigid and soft components. Batteries using soft materials strategy have the same structure as conventional batteries but only the current collectors are replaced. Hence, the specific energy of these flexible Li batteries (FLBs) relates to the areal density of current collectors. Unfortunately, most works reported thick and heavy current collectors in consideration of mechanical reliability and electrical conductivity. In this regard, the metal-on-plastic method was proposed to obtain superlight current collectors with enough mechanical and electrical properties. Specifically, Cu and Al

were coated onto Polyimide (PI) film by the sputtering method. The specific energy of batteries using Cu/PI and Al/PI with sandwich structure increases by 15%-25% for different battery systems.²⁰

Compared to plastic film, textiles are more competitive regarding mechanical performance.²¹ They are well-known for reliable wearability for thousands of years. By incorporating conductive materials, conductive textiles show advantages not only on flexibility but also the battery performance.²² Improved charge transfer kinetics are favored by three-dimensional constructions of textiles so that the rate capability as well as the cyclic stability are enhanced. However, textile-based current collectors still suffer from high electrical resistance and low energy density. For the former, the polymer-assisted metal deposition (PAMD) method is a suitable solution as it allows the formation of a highly conductive metal coating tethered by a polymer interlayer.²³ The inferior energy density is originated from the application of thick fabrics and low packing density of porous textiles in which much space cannot be totally filled with active materials. Hence, the proportion of inactive space and weight in textile-based electrodes needs to be cut for improvement in energy density.

1.2 Research Objectives.

The research focuses on fabricating high-energy FLBs by using superlight textile-based current collectors. Here, superlight glass fiber (GF) fabrics and polyethylene terephthalate (PET) fabrics were chosen as demos to show the application potential of textile-based FLBs. The PAMD method was conducted to develop highly conductive and mechanically robust conductive metal layer onto fabrics. In detail, the objectives are listed below:

1. To prepare highly conductive and superlight fabrics by the PAMD method. The balance between the areal density and conductivity should be optimized by controlling the electroless deposition (ELD) conditions.
2. To improve the anodic stability of the textile-based current collector by using the Ni/P composite coating.
3. To characterize the side reactions triggered by polymer-based fabric substrate and to propose the protection method on the anode side.
4. To assemble highly flexible and energy-dense LIBs.

1.3 Research Originality

As mentioned, there is a trade-off between energy density and flexibility for FLBs. Replacing rigid metal foils with soft materials seems a simple and effective way which favors the scale-up production of FLBs. Among different materials used for fabricating the FLBs, conductive fabrics are the most promising candidate because of their advantages in mechanical robustness and high surface area for charge transfer. In consideration of the cost and ease of mass production, metal-coated fabrics are promising to be commercialized for FLBs in the future. Although hundreds of works have reported textile-based FLBs, their fabrics are heavy and thick, leading to low energy density. In addition, side reaction potentially introduced by the fabric substrate is a severe issue for the practical application of FLBs, however, almost no researches focus on it. In this regard, this research develops scalable methods to fabricate superlight and ultrathin fabric-based current collectors. Moreover, the potential issues that influence the full cell's performance are detailed and discussed. Related protection methods and the corresponding mechanisms are provided.

First, we report the development of a new type of superlight and electrochemically stable current collector, metallic glass fiber fabrics (MGFs). It is well known that GF is widely used as a low-cost and stable insulating material because it has many advantages, such as high mechanical properties, chemical stability, and fire retardancy. The conformal and highly conductive metal layers were deposited onto the GFs by the PAMD method. The introduction of the polymer interlayer ensures a better interfacial binding state between the metal layer and the fabrics, leading to mechanically durable conductive fabrics. FLBs using MGFs as current collectors show improved energy density thanks to the much lighter textile-based current collectors compared to the heavy Cu and Al foils.

Then, we develop a high-voltage fabric-based current collector by using a stable coating material, the Ni/P composite. It was found in the first work that Ni-coated GF fabric (NiGF) is unstable at a potential higher than 4 V (vs. Li/Li^+). It is not eligible for lithium cobalt oxide (LCO), lithium nickel cobalt manganese oxide (NCM) and other high-voltage cathode materials. The instability of NiGF originates from the oxidation of Ni. In this regard, we replace the Ni coating with the Ni/P composite, which has been proven more chemically and electrochemically stable. By further protection of the atomic layer deposition (ALD) method, the full cell using Ni/P coated GF fabrics (NiPGF)/NCM works stably with high flexibility. This coating and subsequent techniques can easily be transplanted to other substrates for the preparation of high-voltage current collectors, for example, a three-dimensional (3D) designed structure.

At last, metal-coated PET fabrics (MPETs) with better mechanical deformability and lower areal density are proposed to further prompt the energy density of FLBs. Different from the GF, PET itself has excellent mechanical properties, especially for the elongation at the break. In addition to the braided structure, PET fabrics are mechanically strong and reliable. However, we found PET is not electrochemically stable on the anode side, which may also be an issue for other polymer candidates. Herein, the degradation of PET in the battery system is monitored and the reaction mechanism is clarified. A corresponding solution, the additional electroplating is used and proved to be effective for protecting the PET substrate. With lower areal densities of 2.1 and 2.7 mg cm⁻² for MPETs, the energy density can be further improved to 207 Wh kg⁻¹, 5.1% higher than MGF-based full cell. The better mechanical performances endow the pouch cell with high flexibility no matter in the segregated-type bending mode or the synchronous-type bending mode. It provides a common strategy for designing polymer fabrics-based current collectors.

In sum, we systematically investigate the application potential of fabric-based current collectors for FLBs. Outstanding improvement in the gravimetric energy density was achieved by the superlight MGFs and MPETs, which represent two kinds of substrate. As paradigms, major considerations were systematically illustrated on the mechanical and electrochemical performances of the substrate and the coating layer. In addition, the possible issues and related solutions were thoroughly discussed. This work blazes a new trail for the future superlight and flexible current collector.

1.4 Outline of the Report

The content of this report is summarized below:

Chapter 1 briefly introduces the background and challenges of FLBs. Then the objectives and originality of this work are demonstrated.

Chapter 2 thoroughly reviews the development from LIBs to FLBs, including the theoretical evaluation on the performances of FLBs and strategies for fabricating high-performance FLBs. Then, the advantages, applications and challenges of textile-based current collectors in FLBs are discussed. At last, the pathways for improving energy density are introduced.

Chapter 3 provides the methodology used in this thesis, including the fabrication and protection methods of the fabric-based current collectors, assembly of the coin cell and pouch cell, characterizations on the electrical, mechanical, and electrochemical performances, and flexibility tests for the textile-based LIBs.

Chapter 4 presents the fabrication of the superlight MGFs and their application for current collectors in a FLB. The trade-off between the areal density and conductivity was optimized. Then, improved energy density and flexibility by using MGF-based current collector are clarified by detailed calculation.

Chapter 5 develops a high-voltage textile-based current collector using the Ni/P composite as the coating layer. The anodic stability and other electrochemical

performances were thoroughly characterized. Then, the further protection of the full cell using NiPGF was realized by the ALD method. The underlying failure and protection mechanism are analyzed.

Chapter 6 illustrates the preparation and characterization of the superlight PET fabrics-based current collectors. The side reactions introduced by PET substrate in the battery system are systematically discussed. Then a simple solution was produced to protect the substrate by additional electroplating. Finally, we present a highly flexible, high-energy LIB using PET fabrics-based current collectors.

Chapter 7 concludes the results of the projects and gives an outlook on the further development of fabric-based current collectors for high-energy FLBs.

Chapter 2. Literature Review

In this chapter, the background of Li-ion batteries (LIBs) and the origin of flexible LIBs (FLBs) are introduced firstly. Then, the theoretical evaluation of performances and the development of FLBs are presented. Textile-based electrodes showing superiority in the fabrication of FLBs are thoroughly discussed. At last, the pathways to improve energy density of LIBs are reviewed.

2.1 Overview of LIBs and FLBs.

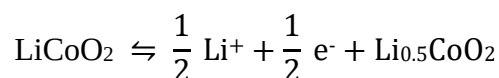
2.1.1 Background of LIBs

In the era of the rapid development of electronic techniques, high-performance energy storage devices are urgently required to meet the requirement of different electric-driven systems, such as portable electronics and electric vehicles (EVs). LIBs have an unrivaled combination of high energy and power density among different battery systems.¹⁰⁻¹² In addition, it has superior features of stable cyclic performance, low self-discharge rate, and no memory effect.²⁴⁻²⁶

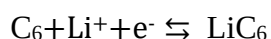
The story is started with the element Li, which has the lowest atomic weight of 6.95 and the lowest density of 0.534 g cm^{-3} among all the metals. It means that a unit of Li is oxidized by losing many electrons, which results in an ultrahigh gravimetric capacity of 3860 mAh g^{-1} . Combined with the extremely low reduction potential of -3.0564 V versus standard hydrogen electrode (SHE),²⁷ a high energy density can be expected in battery chemistry containing Li.²⁸ Primary Li batteries (LBs) faced to the world during the 1970s, and specific classification and characterization are well described in

numerous records.²⁹⁻³¹ Researchers tried their best to make rechargeable LBs using Li metal as the anode. Still, they failed due to the safety problem and short cyclic life originating from the overactive Li metal.^{32, 33} The commercialization of LBs stagnated for a time until the introduction of graphite as the anode material. It propelled the evolution of LBs, making them with much better safety and cycle life and was finally commercialized in 1991 by Sony.

A representative commercial LIB system consists of a graphite (Gr) anode and a lithium cobalt oxide (LCO) cathode, as illustrated by Figure 2.1. The energy storage for LIB is realized by Li-ion intercalation-de-intercalation cycles between active materials in the anode and cathode. In view of the stability of cathode material and electrolyte, the reaction in the cathode is:



The cut-off voltage used here is 4.2V because increasing the upper voltage with further extraction of Li^+ will cause the collapse of the structure for LCO. In this state, only half of the Li source (140 mAh g^{-1}) is extracted from LCO by the first-order phase transition between LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$.³³ Correspondingly, a reaction occurs in the anode is:



The intercalation of Li into Gr was accomplished with the formation of LiC_{24} , LiC_{27} , and LiC_{12} through a first-order phase transition.³⁴ The commonly used electrolyte, carbonates, are unstable at the potential below $\sim 1 \text{ V}$ (vs. Li/Li^+). Hence, the electrolyte is reduced in the first cycle, forming a protective layer on the Gr electrode. This solid electrolyte interface (SEI) film is conductivity for Li ions but insulative for electrons, preventing further reduction of electrolyte.³⁵ Benefiting from this particular interface layer, LIBs can run stably for hundreds of cycles.

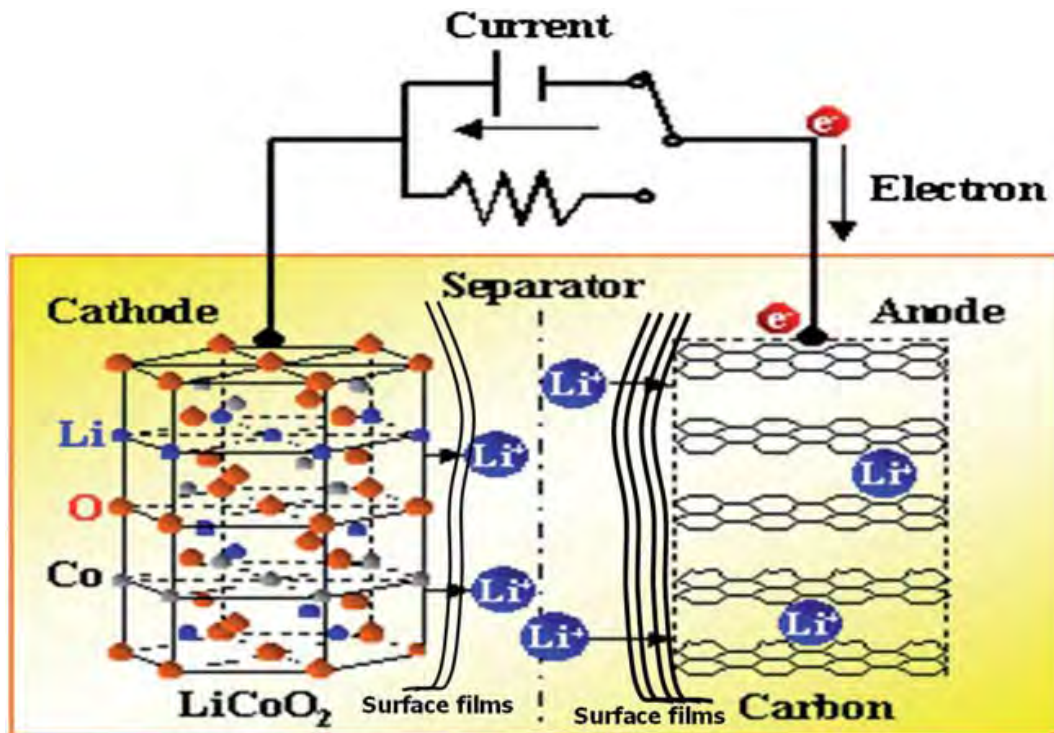


Figure 2.1 Schematic of the LIB using LCO and Gr as active materials. Reproduced from ref. [25].

2.1.2 Origin of FLBs

Nowadays, flexible or wearable electronics have attracted much attention due to their potentials in different areas, including sensors, displays, health care, or even aerospace.³⁻

⁹ All electronic systems cannot work without a power source, but traditional LBs can only meet the requirements of portable electronics. It is decided by the conventional structure of Li batteries and the properties of components. As shown in Figure 2.2, a commercial prismatic battery consists of four major components: the electrodes, separators, electrolyte, and packages. Commercial electrodes are made by coating active material slurry onto current collectors. In the composite electrodes, all the elements including active materials, metal foils, and conductive agents are rigid in

nature except for the binder. To pursue a high capacity, electrodes and separators are alternatively stacked to form a thick and rigid structure. In addition, outer packages are usually tough and rigid to protect the internal battery system.



Figure 2.2 Schematic structure of a rigid prismatic battery.

To get an integrated flexible system, the selection of materials and integration of these components in LBs should be reconsidered to meet the increasing demand for flexibility. Regarding the end-use of these flexible batteries in different areas, FLBs are requested to stably provide power during bending, twisting or other deformations. Therefore, the challenges for FLBs refer to the dynamic mechanical and electrochemical stability of the battery system.

2.2 Performance Evaluation of FLBs

The urgent demand for FLBs prompts more researchers to focus on the topic, leading to a mushroom increase in the works of different kinds of FLBs. However, different

from the mechanical property or electrical property, flexibility is more challenging to evaluate, especially when comparing various works because the test conditions are different. Moreover, in general situations for FLBs, flexibility is significantly influenced by the areal capacity, i.e., the thickness of the active material composite layer. Hence, it is necessary to establish a performance evaluation metric for a better understanding of the development of FLBs.

2.2.1 Metric for Measuring Flexibility of FLBs

In the last ten years, much effort has been put into the structure design and materials to enhance the flexibility of lithium batteries. However, it is hard to systematically compare different works regarding flexibility because there is no fixed standard.³⁶ In most cases, the bending test is the most popular characterization, and bending radius is the only indicator to demonstrate flexibility.¹⁴ Actually, it is somehow misleading because the maximum localized strain not only depends on the radius but also the other factors.¹⁷

Li et al. proposed using bending angle (θ), bending radius of curvature (r) and device length (L) to evaluate the bending durability (Figure 2.3).³⁷ The basis of utilizing these three factors is stated as follows: They don't have absolute correspondence with each other. For example, L can differ when the bending radius r and bending angle θ are set. A larger object performs better under bending as stress is not so concentrated in a localized region. They constructed a Zn-MnO₂ battery and polypyrrole (PPy)-based supercapacitors to study the influence of bending parameters. The results showed that three parameters independently influence the electrochemical performances of flexible energy storage devices.

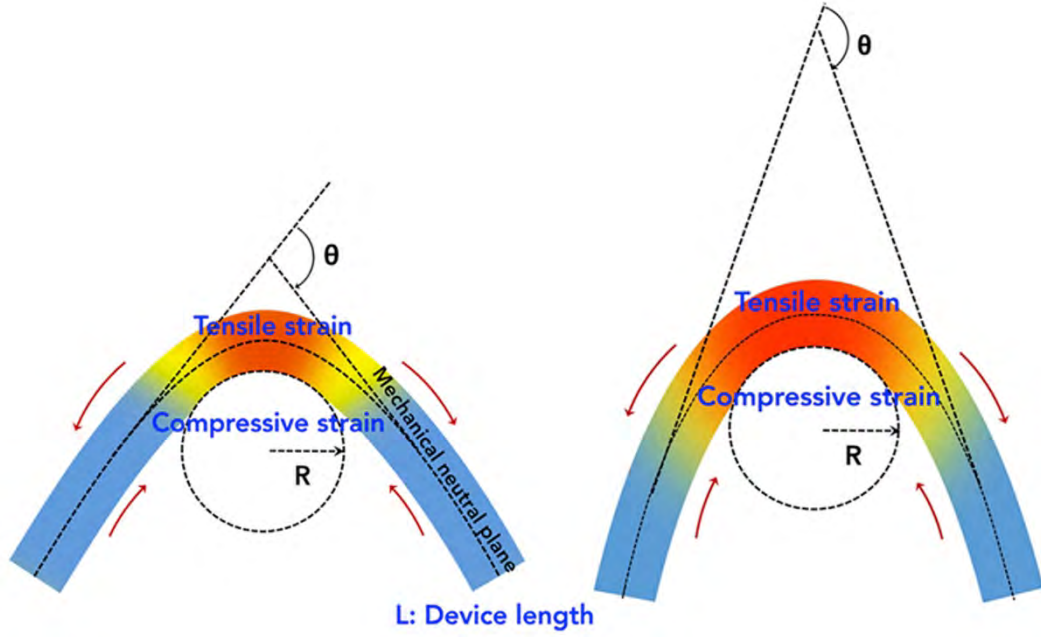


Figure 2.3 Schematic of structures and three key parameters (L , θ , and R) used to describe the bending state. These two pictures demonstrate that these three factors have no strict relationship with each other. Reproduce from ref. [37].

Flexibility can also be reflected by the minimum bending radius of curvature (r_b , i.e., the breaking bending radius of curvature). In this regard, flexibility f is defined as:

$$f = 1/r_b \quad \text{Equation 2.1}$$

Then the maximum strain (ε) of the out layer can be calculated by:

$$\varepsilon = [2\pi (r_b + h/2) - 2\pi r_b] / 2\pi r_b = h/2r_b \quad \text{Equation 2.2}$$

where h is the thickness of the device. Hence, the maximum strain (ε) at the failure of a material can be regarded as the only criterion for the laminar slab model.^{17, 38, 39} As proposed by the institute for printed circuits, r should be lower than ten times T (IPC-2292 standard) for a flexible device. It means every component of a flexible battery should have strains larger than 5%.

The mechanical properties of commonly used battery materials are shown in Table 2.1. It is meaningless to discuss the flexibility of electrolyte because it is in a liquid state. Separators are made of polyethylene (PE) or polypropylene (PP) whose yield strains are larger than requested. However, traditional current collectors (metal foils) and active materials are rigid in nature, with little deformability. The composite electrode layer is a porous layer composed of rigid active materials, conductive agent and elastic binder. Table 2.2 presents the reported mechanical properties of the composite electrode layer. These values differ largely between different works because of different test methods and simulation methods were employed. Even so, a common conclusion was claimed by most works that the mechanical failure of the electrodes starts from the Al current collector and then the Cu current collector.⁴⁰⁻⁴² In other words, the composite electrode layer has a better deformation ability than current collectors.

Table 2.1 Mechanical properties of materials commonly used in battery components.

Materials	Young's modulus (GPa)	Yield strain (%)	Tensile strength (GPa)	Ref.
Cu foil ^a	70-102	0.5-1.0	0.1-0.3	[43]
Al foil ^a	69	0.2	0.1	[44]
LiCoO ₂ ^b	264	0.15	40	[45]
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	198	0.3	60	[40, 46]
Graphite ^b	109	0.5	55	[40, 46]
LiFePO ₄ ^b	312	0.16	50	[46]
Polypropylene ^c	1.2-1.7	5	0.02	[47]
Polyethylene ^c	0.8-1.2	10	0.01	[47]

^a Typical material used for current collectors, ^b Typical active materials, ^c Typical material used for separator. Reproduced from ref. [17]

Table 2.2 The mechanical properties of composite electrode layers.

Composite electrode layer	Young's modulus (MPa)	Yield strain (%)	Tensile strength (MPa)	Ref.
Graphite	674	/	2.43	[40]
NCM	609	/	2.56	
Graphite	2500	3.8	~10	[41]
NCM	5900	0.75	~17	
NCM	15-280	0.6-1.5	0.22-1.7	[42]

Further formula derivation can be conducted by transferring the strain at failure (ε_y):

$$f = 1/r_b = (2/h) \varepsilon_y = (h/2) (\sigma_y/E) \quad \text{Equation 2.3}$$

where the σ_y is the yield stress, and E is Young's modulus. The left ($h/2$) represents the geometric parameters of the test condition, while the right (σ_y/E) correlates to the mechanical property of the material. At a fixed thickness of h , the flexibility can be evaluated by the flexibility figure of merit (f_{FOM}):

$$f_{\text{FOM}} = \sigma_y/E \quad \text{Equation 2.4}$$

As shown in Figure 2.4, compliant (low Young's modulus) and strong (high yield strength) means high flexibility. Just the same as traditional cognition, polymers and elastomers, as well as some nanomaterials are flexible.

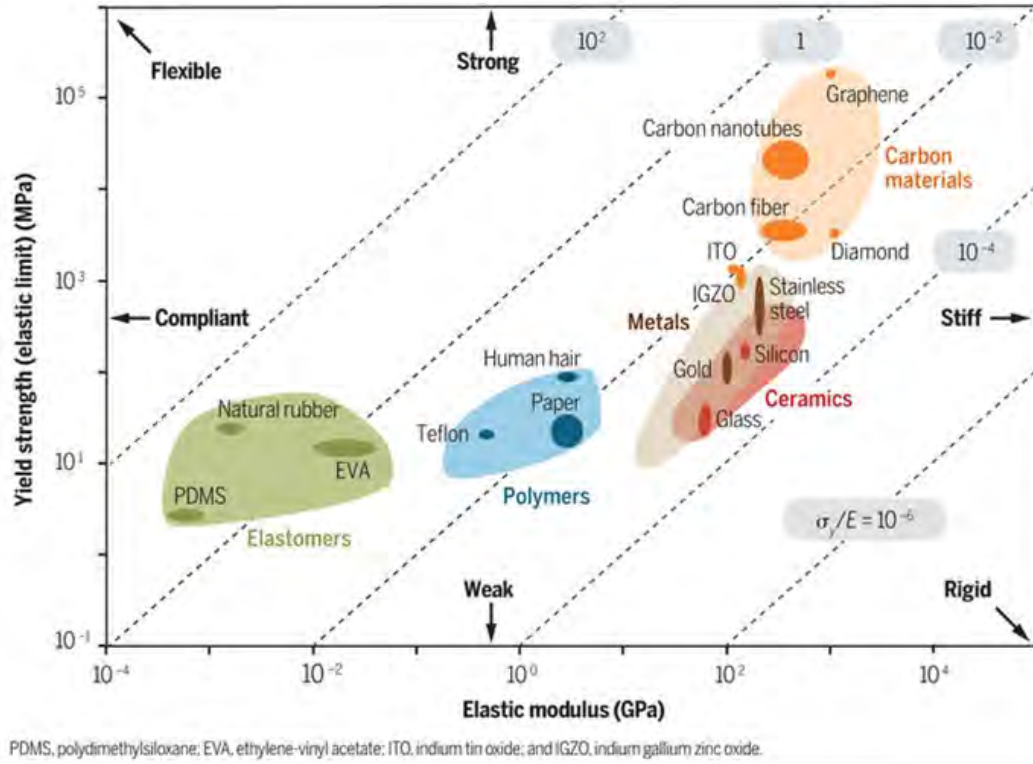


Figure 2.4 Flexibility figure of merit (fFOM) for different materials. Reproduced from ref. [38].

2.2.2 Benchmark for Overall Performance of FLBs

Energy density is the most critical parameter for all batteries. A fair evaluation of a FLB can focus not only on the flexibility but also the energy density because the final task of FLB is to power the electronics. Figure 2.5a illustrates the least requirements on the energy density and strain for some appealing applications, such as the bendable phone and roll-up displays.

Given the hardness for benchmarking the performance among the mass data reported in different manuscripts, a figure of merit (FOM) is suggested to compare the

combination properties quantitatively.³⁹ As mentioned above, ε is a more appropriate parameter to estimate flexibility than r . Except for flexibility, energy density (E_v) is another key metric to consider when evaluating a flexible battery. Hence, the evaluation of the performance of flexible batteries (fb) should take both E_v and ε into consideration:

$$fb = \varepsilon E_v = (h/2r)(CV/Ah) = (CV/A)/2r = 1/2 (E_a/r) \quad \text{Equation 2.5}$$

where C , V , and A are the capacity, nominal voltage, and projective area of the battery cell, respectively, and E_a is the areal energy density of the battery.

The FOM of a flexible battery can then be given by E_a/r :

$$fb_{\text{FOM}} = E_a/r \quad \text{Equation 2.6}$$

For most reported flexible batteries, r during the bending state is usually provided, and E_a can be calculated from the areal capacity and voltage of the battery. FOM chart can be plotted to evaluate the performance of flexible batteries (Figure 4). It is especially suitable to compare the laboratory data because the areal energy is more available than energy density or specific energy calculated by detailed parameters. In addition, the FOM allows facile estimation on the suitability of laboratory results to industry requirements.

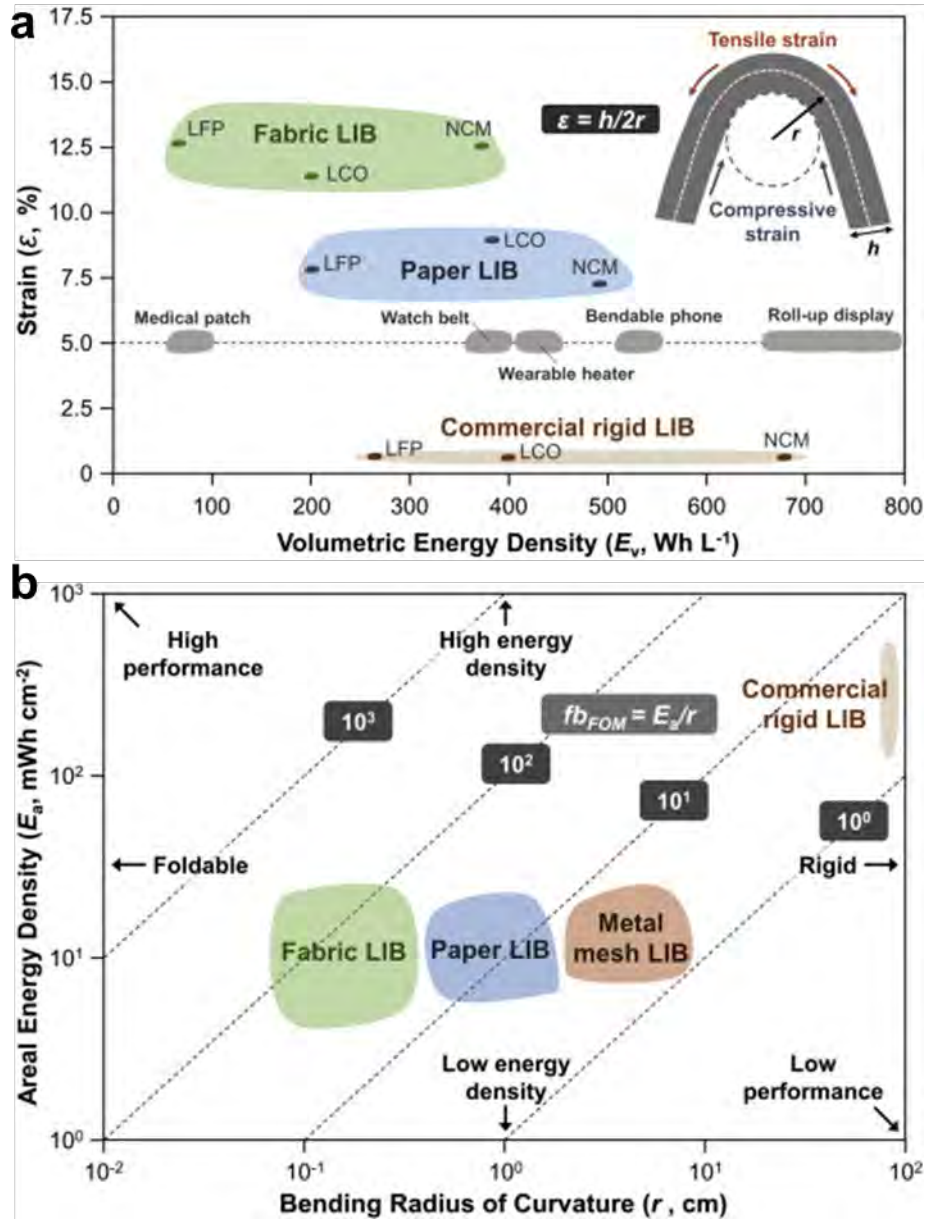


Figure 2.5 a) Strain (ϵ) as a function of volumetric energy density (E_v) for batteries, showing the request of some typical applications and the current development. b) A FOM for flexible batteries considering both flexibility and energy density. Reproduced from ref. [39].

2.3 Strategies for Developing High-Performance FLBs

In the practical application of FLBs, not only the essential mechanical performance of the battery components but also the interfacial adhesion between the current collectors

and active material composite layer should be considered. The delamination of active materials during deformations is another major cause for the capacity fade or the failure of FLBs, apart from the fracture of the battery components. To fabricate a high-performance FLB, combination properties of high flexibility and high energy density must be considered simultaneously. At the primary stage of the development, researchers tended to only focus on flexibility but now the energy density gets much emphasis as well. Figure 2.6 presents the representative works of FLBs in the last twenty years.^{15, 48-56} To achieve high flexibility, different methods have been proposed, and they can be classified into two main strategies, namely “soft material” strategy and “soft structure” strategy.

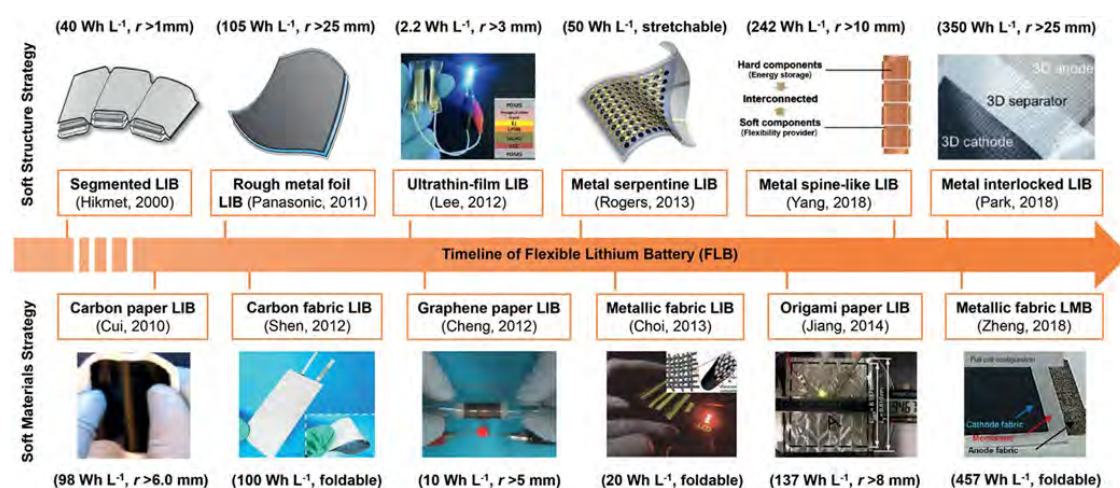


Figure 2.6 Timeline of development for FLBs. Reproduced from ref. [17].

2.3.1 Soft Materials for FLBs

Among different kinds of materials, carbonaceous materials show excellent electrical and mechanical performances simultaneously.^{57, 58} Carbon nanotubes (CNTs) and graphene are representative nanomaterials to fabricate thin, flexible, highly conductive current collectors. As discussed before, thickness is the determinant factor of flexibility.

In addition, current collectors based on carbon nanomaterials are porous in nature, which endows them with better deformability although they are very rigid in nature. Except for CNT⁵⁹⁻⁶¹, graphene⁶²⁻⁶⁵ and carbon fibers⁶⁶⁻⁷⁰, the typical building blocks also include some carbonized polymers, for example, polyacrylonitrile (PAN)^{71, 72} and cellulose⁷³⁻⁷⁵. Hybrid current collectors are also developed in consideration of fully utilizing their advantages. As carbonaceous materials are electrochemically active, researchers also use them as active materials.⁷⁶⁻⁸³ In this section, we will not cover these works and only focus on the applications in current collector.

2.3.1.1 CNT-based Soft Current Collectors

CNT is a 1D nanomaterial with high electrical conductivity and outstanding mechanical strength. It can be easily assembled into different types of current collectors, including films, sponges, and fibers. In 2010, free-standing CNT paper was used as current collectors for both electrodes (Figure 2.7a and 2.7b).⁵¹ The full cell showed an energy density of 98 Wh L⁻¹, and it is stable after 50 bending cycles ($r = 6$ mm). The anode material used in this work is lithium titanium oxide (LTO) which has a high lithiation potential, so the working voltage of the full cell is low. Aligned CNT films collected from the CNT arrays are suitable for the roll-to-roll production and, thus the scalable manufacturing of FLBs. The super-aligned CNT film exhibited better interfacial adhesion between the current collector and the Gr composite layer than the commercial Cu foil.⁸⁴ The better interface connection may prompt the transportation of electrons so that a better rate capability was realized. Moreover, Fu et al. used the super-aligned CNT film as the mechanical scaffold to accommodate the Si and buffer the volume expansion.⁸⁵ It was achieved by electrochemical deposition of Si on the CNT film substrate (Figure 2.7c-e). The porous structure facilitates the electrochemical kinetics

so it showed a high capacity of 1600 mAh g⁻¹ and reasonable cyclic stability. The scalable production of aligned CNT film was presented by Wu et al.⁸⁶ An ultra-large (1800 mm × 1000 mm) film with excellent electrolyte and high conductivity was prepared (Figure 2.7f). The resultant FLB exhibited a large capacity of 700 mAh with superior flexibility. It should be noted that CNT is electrochemically active for Li⁺ as other carbonaceous materials. The proportion of CNTs was very small compared to active materials, or the active materials used in the anode have a working potential range that is not applicable for the intercalation of Li⁺ into CNT in these successful applications of CNT-based current collectors.

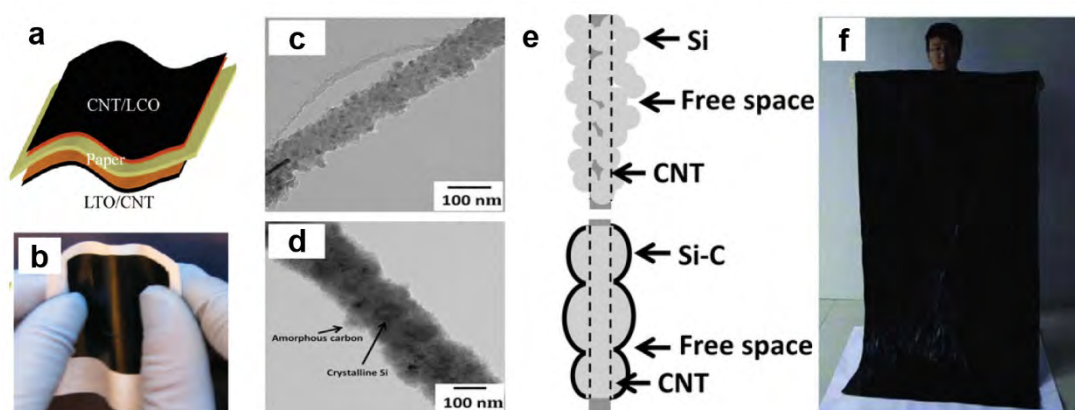


Figure 2.7 a) Schematic and b) photo of the CNT paper-based FLB, reproduced from ref. [51]. TEM images of c) CNT-Si, d) CNT-Si-C and e) corresponding schematic images. Reproduced from ref. [85] f) Photograph of the ultra-large (1800 mm × 1000 mm) aligned CNT film. Reproduced from ref. [86].

2.3.1.2 Graphene-based Current Collectors

Graphene is a 2D nanomaterial that has attracted tremendous attention since it was obtained by the tape method in 2004. Compared to the 1D CNT, the preparation of high-quality graphene film is relatively tough because the 2D sheets tend to shrink in solution

fabrication. In addition, it has relatively high electrochemical activity so it will influence the battery performance significantly if a low-potential anode material is used. Graphene paper was first adopted as the current collector of the V_2O_5 cathode which was grown by pulsed laser deposition (Figure 2.8 a-c).⁸⁷ On the anode side, graphene paper acted as the current collector as well as the active material. The as-prepared flexible battery can operate normally when it was rolled up. However, the areal capacity is low of $15 \mu\text{Ah cm}^{-2}$, and the cyclic stability is not ideal. The vacuum filtration method is an effective way to fabricate highly conductive graphene membranes as 2D graphene tends to spread out.^{88, 89} Then, lithium iron phosphate (LFP) and LTO were also coated onto the membrane by filtration method. Obtained composite electrodes displayed stronger interfacial adhesion and better flexibility than conventional LIBs. Other than the graphene film, another macroscopic structure, graphene foam is relatively better to be used as a flexible current collector (Figure 2.8 d-f).⁵³ The porous structure can not only displays higher flexibility but also endows the foam with fast charge transfer by shortening the diffusion length.^{90, 91} By employing LFP and LTO as active materials, the flexible battery using graphene foam exhibited excellent rate and cycle performance. Also, it could be repeatedly bent at the bending radius of 5 mm without apparent deterioration in capacity.

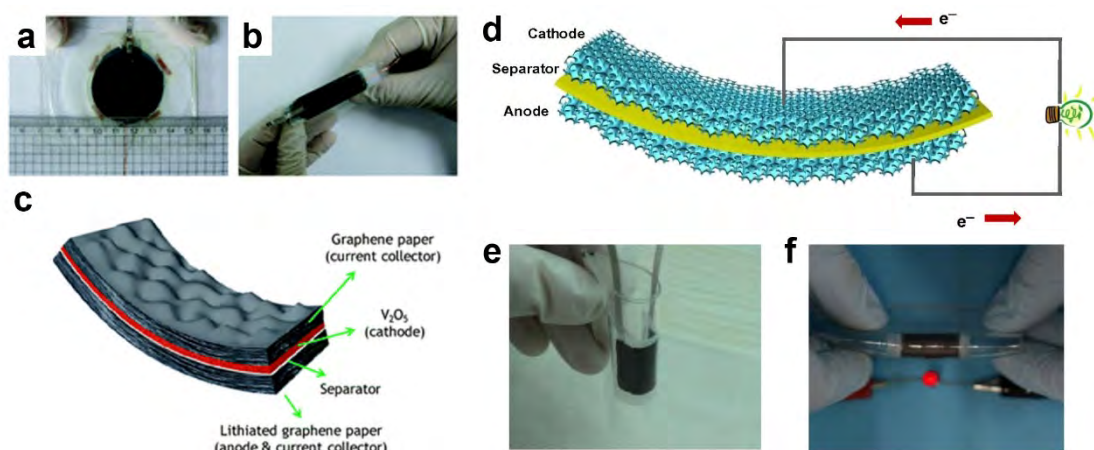


Figure 2.8 a, b) The assembled graphene paper-based FLB at the flat and bending states. c) Schematic drawing of the graphene paper-based FLB. Reproduced from ref [87]. d) Schematic of a flexible battery using graphene foam as current collectors and e, f) photograph of a graphene foam-based battery lighting a red LED device under bending. Reproduced from ref. [53].

2.3.1.3 Hybrid CNT/graphene Current Collectors

Integrating 1D CNT and 2D graphene is believed to take advantage of their merits or even manifest synergistic effect. It was reported that the pillar-like CNTs could prevent the restack of graphene, and the graphene can help CNT uniformly disperse in reverse.⁹² In a typical work, CNTs function as the long-range electron highway, and MgO-derived graphene nanocages accommodate the sulfur powder (Figure 2.9a-c).⁹⁴ Such an all-carbon flexible battery exhibited decent cycle stability (Figure 2.9d) and an outstanding reversible capacity of 750 mAh g⁻¹ at a high rate (Figure 2.9e). A 3D multilayer porous scaffold with CNTs and reduced graphene oxide (rGO) can also be prepared by vacuum freeze-drying (Figure 2.9f).⁹⁵ Active material MnO₂ grew directly on the rGO by hydrothermal method, facilitating the electron transport and structural stability. The unique sandwich structure endows the flexible battery with excellent rate capability and cycle performance (Figure 2.9g).

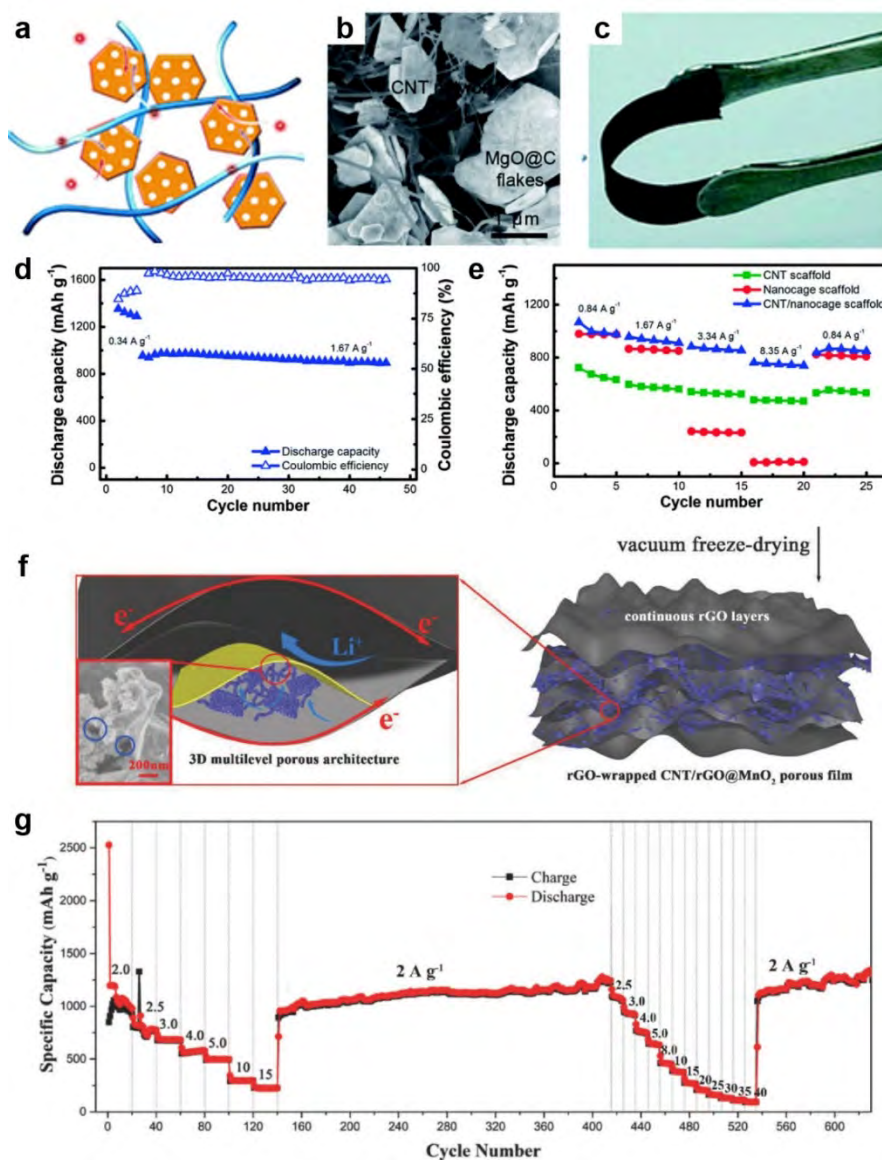


Figure 2.9 a) Schematic of an all-carbon scaffold used for accommodating S cathode. b) SEM image of the CNT/MgO@C composite. c) optical image of the flexible S cathode membrane. d) Cycle and e) rate performance of the flexible S electrode. Reproduced from ref. [94]. f) Schematic for the preparation of rGO-wrapped CNT/rGO/MnO₂ porous (GCMP) film and g) electrochemical rate performance of GCMP electrode. Reproduced from ref. [95].

2.3.1.4 Carbonized Polymer-based Current Collectors

Carbonization of polymer is a facile method to fabricate flexible current collectors in

LIBs, especially for those with complex or specific structures in consideration of easy processibility for polymer materials. For instance, Wu et al.⁹⁶ reported a flexible battery by the carbonization of porous cellulose and subsequent infiltration of the active materials, Li_2O (Figure 2.10a). By inheriting the intrinsic porous structure of cellulose, the as-prepared electrode has highly conductive networks and numerous micro-holes, which are beneficial for electrochemical kinetics. In addition to the uniform distribution of Li_2O , the flexible battery showed stable cycle performance at high mass loading. The combination of electrospinning and carbonization for polymer provides a new pathway to manufacture current collectors with high flexibility. A flexible and free-standing $\text{Nb}_2\text{O}_5@\text{MoS}_2@\text{C}$ carbon nano-fibers (CNFs) paper film was obtained by successive hydrothermal treatment using electrospun PAN fibers as substrate (Figure 2.10b).⁹⁷ The composite electrode allowed the release of respective advantages of high stability for Nb_2O_5 and hard carbon, high capacity of MoS_2 . Wang et al.⁹⁸ employed the electrospray of Si solution with the electrospinning of PAN fibers to fabricate a Si/C fiber film with uniformly distributed nano-Si clusters (Figure 2.10c and 2.10d). A better interface contact between Si and current collectors was achieved, and the volume expansion could be relieved by CNFs. As a result, the flexible electrode exhibited outstanding cyclic performance with an initial capacity of 1600 mAh g^{-1} , which was not influenced by the mass loading.

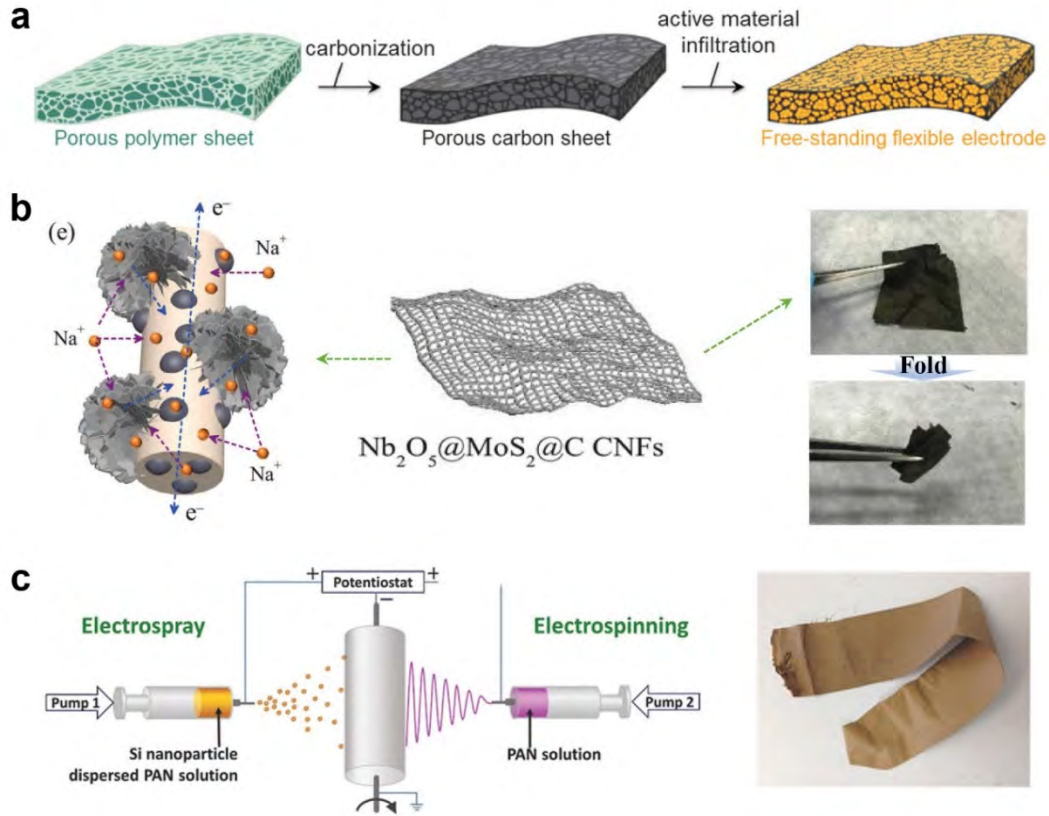


Figure 2.10 a) Synthesis flows of carbonized porous cellulose sheets for the flexible sulfur electrodes. Reproduced from ref. [96]. b) Schematics of the nanostructure of $\text{Nb}_2\text{O}_5@\text{MoS}_2@\text{C}$ CNFs fil and its corresponding photographs. Reproduced from ref. [97]. c) Synthesis process and photograph of the flexible Si/C electrode made by simultaneous electrospinning and electrospray. Reproduced from ref. [98].

2.3.2 Soft Structure Design for FLBs

Apart from applying flexible materials, structure design for FLBs is another important research area. The flexibility is a parameter for the macroscopic battery, not only determined by the intrinsic mechanical properties of components. For a simple instance, a rigid matter can be flexible if the thickness is very low. In addition, the distribution of external stress and strain can be reorganized by unique structures so the whole device shows flexibility within which rigid components are protected.

2.3.2.1 Design of Wire-type Structure

The wire-type structure has two-dimensional flexibility because of its 1D characteristic (low thickness on two-dimensional).⁹⁹ Based on the different spatial arrangement of the battery components, the wire-type battery can be classified into three kinds: parallel configuration, twisted configuration, and coaxial configuration (Figure 2.11a).¹⁰⁰ The first wire-type FLB was reported by Kwon et al. by using the hollow Ni-Sn alloy deposited Cu spiral as inner anode and a composite cathode on Al wires (Figure 2.11b and 2.11c).¹⁰¹ This cable-shaped FLB could be easily rolled up or twisted (Figure 2.11d) and presented stable output voltage under bending conditions (Figure 2.11e). The complex configuration was then simplified by employing CNTs as current collectors and gel electrolyte. Different active materials, including MnO₂, LTO, LiMn₂O₄, Si, and MoS₂ were incorporated with CNTs fibers to assemble the wire-type battery.¹⁰²⁻¹⁰⁵ By overtwisting the CNT fibers together, springlike CNT fiber was obtained to endow the electrodes with stretchability (Figure 2.11f-h).^{106, 107} The relief of the twisting state during elongation allowed the electrode to be easily stretched and recovered (Figure 2.11i-k). This stretchable electrode exhibited a capacity retention of 85% even at a 100% elongation.

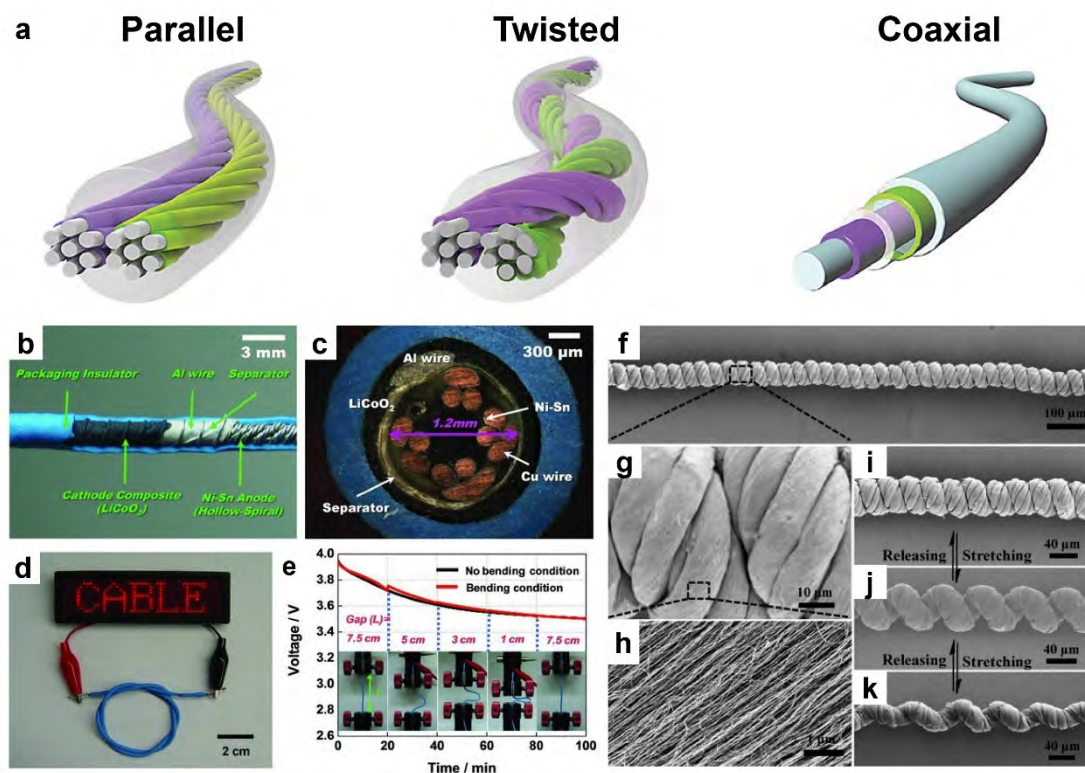


Figure 2.11 a) Schematic of wire-type FLBs with different configurations. Reproduced from ref. [100]. b) Lateral and c) cross-sectional view of the first wire-type FLB. d) Photograph showing the flexibility of the FLB. e) Discharge curves of the cable-shaped FLB during different bending statuses. Reproduced from ref. [101]. f-h) SEM images of a springlike fiber at different magnifications. i-k) SEM images of a fiber at different strains 0 %, 50 %, and 100 %. Reproduced from Ref. [106].

However, due to the relatively complex structure, the production of wire-type batteries is limited. In addition, long wire-type FLB was believed to have high internal resistance, which will be harmful to the electrochemical kinetics of the battery. In 2021, He et al. reported a production method of fiber FLBs with a set of large-scale equipment (Figure 2.12a-e).¹⁰⁸ Totally contradicted to the expectations, a hyperbolic cotangent relationship between the internal resistance and the length of the fiber battery was observed, manifesting that the resistance decreased first with the increase of length and then kept

steady. It provides the theoretical base for the development potential of long-fiber batteries. After optimizing the manufacturing techniques, the FLB exhibited a high capacity of 90.5% after 500 charge/discharge cycles (Figure 2.12f).

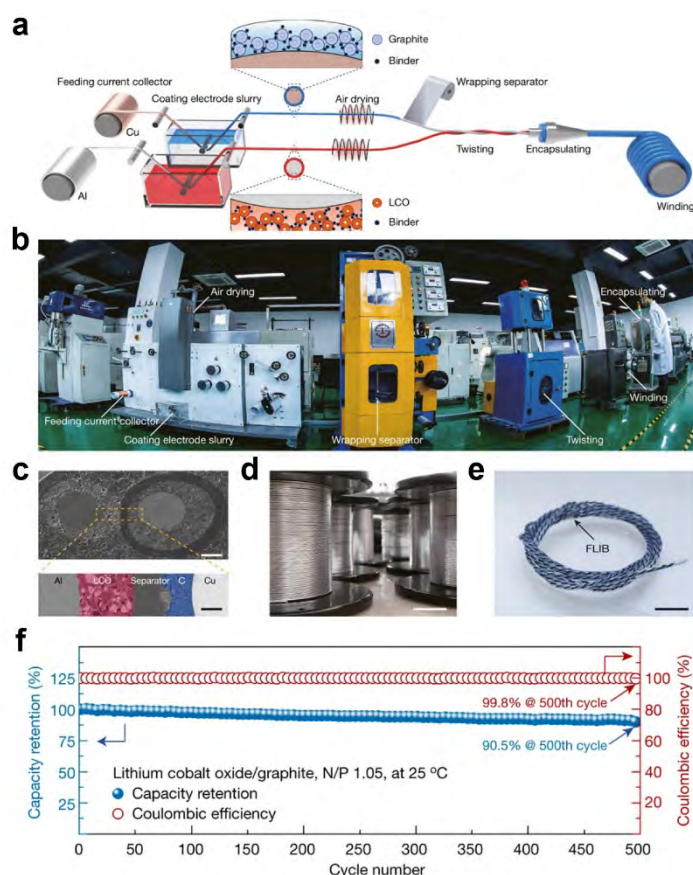


Figure 2.12 a) Schematic of continuous fabrication for FLBs. b) Photograph of the industrial-scale fabrication line of FLIBs. c) Cross-sectional SEM image of the wire-type FLB. d) Reels of the wire-type FLB. e) Photograph of FLB with a length of 1 m. f) Cycle performance of the wire-type FLB. Reproduced from ref. [108].

2.3.2.2 Design of Origami and Kirigami Structure

Origami and kirigami are traditional handcraft art full of the wisdom of the ancients. Many works borrowed the concept of origami to make flexible electronics by suitable pattern design.¹⁰⁹⁻¹¹² This strategy bases on the relationship between the pattern and the stress distribution. Song et al.⁵² applied this concept in conventional planer LIBs with

CNT-based current collectors (Figure 2.13a). It was realized by folding the battery based on specific origami patterns of Miura-ori in which parallelogram faces are connected by ‘mountain’ and ‘valley’ creases (Figure 2.13b). In this design, deformations only occurred in these creases while the parallelogram faces maintained undeformed. As a result, the origami battery can normally work under a complete compress state, even showing a higher areal capacity than the flat state.

Although paper-folding is a facile but effective way to fabricate FLBs, it should be mentioned that the pre-folded creases highly limit the deformation of the battery. In this regard, the kirigami (i.e., folding and cutting method) concept was then borrowed to fabricate FLB using metal foils as current collectors.¹¹³ By using the new “plastic rolling” deformation mechanism, the kirigami FLB showed reasonable cyclic stability, with 85% capacity retention and 99.8% coulombic efficiency (CE) after 100 cycles. Similar kirigami patterns could also be obtained by printing technology, as shown in Figure 2.13c.¹¹⁴ The simple pattern design enabled the electrodes with outstanding flexibility on different deformation types including bending, twisting, and stretching (Figure 2.13d and 2.13e). After 500 stretching cycles, the full cell with kiragami electrodes exhibited a discharge capacity of over 100 mA h g⁻¹ after 100 discharge/charge cycles.

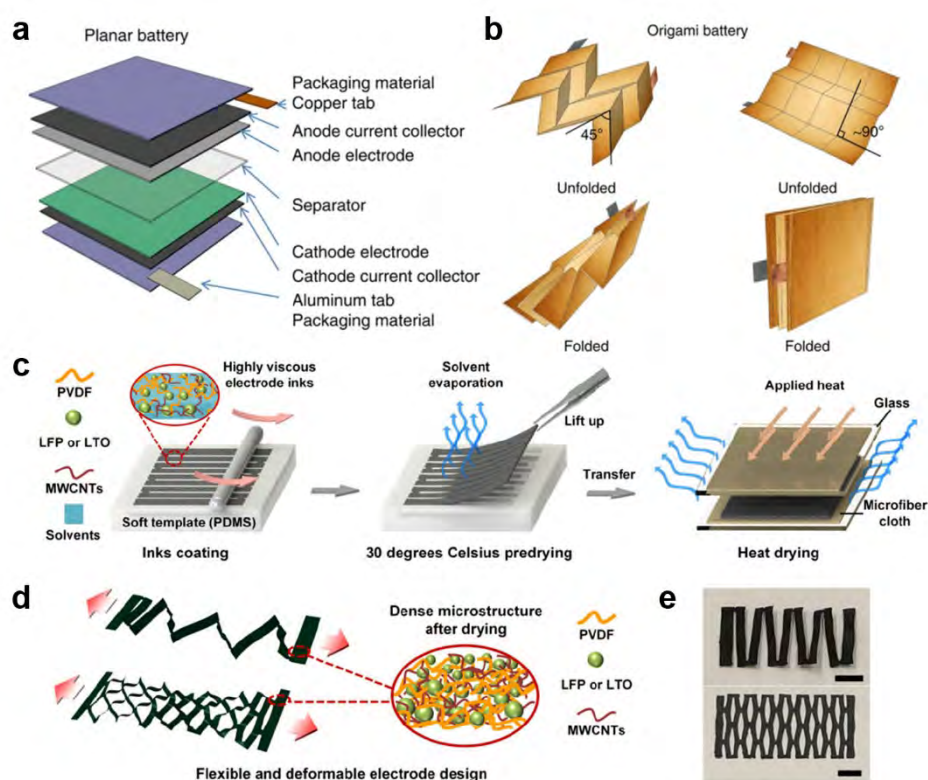


Figure 2.13 a) The configuration of the conventional planar battery. b) Schematic of origami LIBs. Reproduce from ref. [52]. c) Schematic fabrication process for the kirigami-based electrodes. d) Illustration of the deformable kirigami-based electrodes under stretched states. e) Photographs of the kirigami-based electrodes with different patterns. Reproduced from ref. [114].

2.3.2.3 Design of Segmented Structure

Segmented structure means that the whole battery is composed of different segments, which are usually rigid parts for energy storage and soft part for buffering the external stress. In 2013, Prof. Rogers and his colleagues designed a structure in which many small electrodes are connected by a serpentine-like circuit (Figure 2.14).⁴⁸ The self-similar structure endowed the battery with a stable performance during stretching. Specifically, serpentine-like circuits on the soft substrate can maintain stable transportation of electrons under harsh deformations. The rigid parts, i.e., small

electrodes have minimal deformation even when the whole battery is under extreme stretching. It should be noted that the final battery includes much inactive volume and weight, which leads to a low energy density of $\sim 50 \text{ Wh L}^{-1}$.

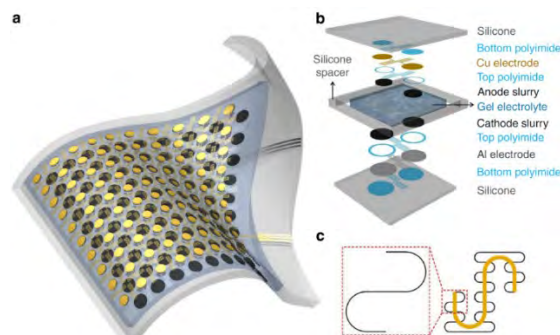


Figure 2.14 a) Schematic of a flexible battery with a structure that a serpentine-like circuit connects many small electrodes, b) exploded view of the flexible battery, and c) illustration of the serpentine-like circuit with self-similar geometry. Reproduced from ref. [48].

Another representative structure is a spin-like structure (Figure 2.15a).⁵⁰ In this design, the rigid part is fabricated by rolling the cathode and anode together to store energy, while soft components act as marrow to withstand the applied stress and strain. As the volume fraction of the soft connection is very low, this battery exhibited a high energy density of 242 Wh L^{-1} , almost 85% of that in conventional packing. No apparent influence on the capacity was observed when applied the flexing and twisting deformations (Figure 2.15b), demonstrating that the spin-like battery has high flexibility with stable electrochemical performance. It should be noted that the flexible dimension is limited because of the spin-like structure (Figure 2.15c). Recently, a similar work mimicking the human joint to fabricate FLB was reported (Figure 2.15d).¹¹⁵ Battery using this configuration can withstand flexing, folding, twisting, stretching, and other harsh deformations (Figure 2.15e and 2.15f). There is no noticeable change in exertion of capacity during these deformations. In addition, the

joint-like FLB showed stable power output at dynamic (applied deformations and charge/discharge process are simultaneous) bending and twisting tests. Benefiting from the low fraction of inactive components, it shows a high energy density of $\sim 370 \text{ Wh L}^{-1}$. Other interesting configurations, including the wavy structure,¹¹⁶ zigzag-like,¹¹⁷ crocodile skin-like¹¹⁸ and accordion-like¹¹⁹ structure, were presented to prepare high-performance FLBs.

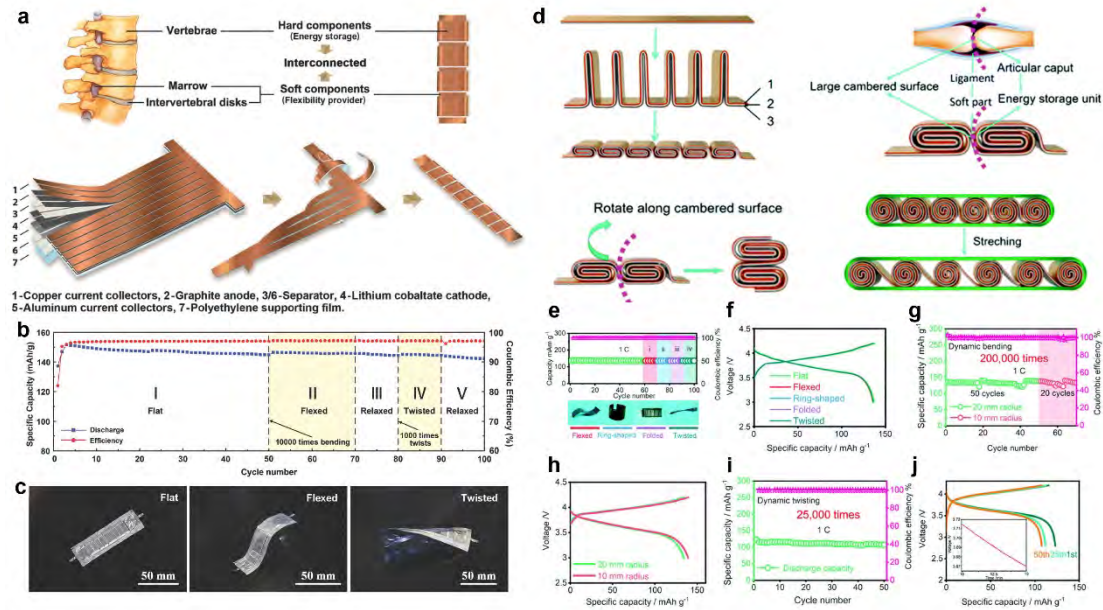


Figure 2.15 a) Schematic fabrication process of the flexible electrode with spine-like structure. b) Cycle performance of the spine-like battery in different deformations at 0.2 C. c) Photographs of the spine-like battery in flat, flexed, and twisted states. Reproduced from ref. [50]. d) Schematic fabrication process of the flexible electrode with joint-like structure. e) Cycle performance of the joint-like cell in different deformations and (f) corresponding galvanostatic charge-discharge (GCD) curves. (g) Cycle performance of the joint-like battery in the dynamic bending test, and (h) the corresponding GCD curves. (i) Cycle performance of the joint-like battery in the dynamic twisting test, and (j) the corresponding GCD curves. Reproduced from ref. [115].

2.4 Textile-based Flexible Batteries

Textiles are well-known for their reliable wearability for thousands of years. The robust mechanical property originates from the combination of raw material's nature property and designed hierarchical structure. Such flexible feature makes textiles promising to be used as the substrate for current collectors, which is the most prone to failure during deformations. With the development of textile-based batteries, more advantages of conductive textiles in battery systems were explored.

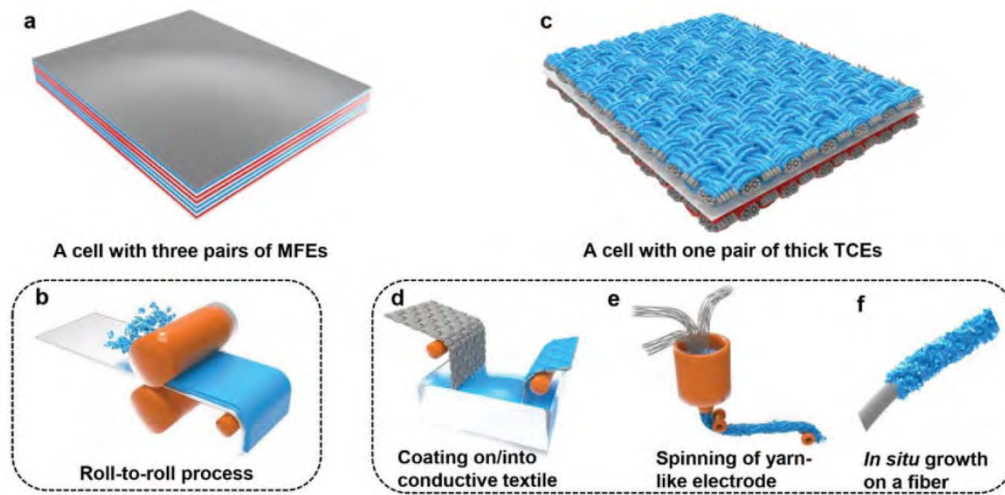


Figure 2.16 Cell structure of stacked a) metal-foil-supported electrodes (MFEs) and b) textile composite electrodes (TCEs). Fabrication of c) MFEs via roll-to-roll method and TCEs via d) coating, e) spinning, and f) in-situ growth. Reproduced from ref. [22].

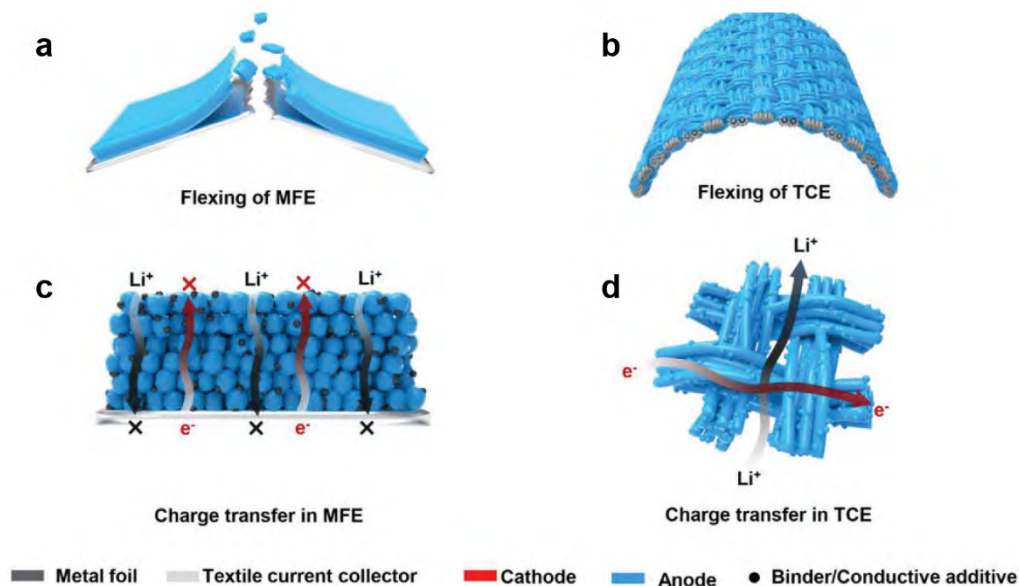


Figure 2.17 a) Fracture of the MFE or delamination of active material slurry when subject to bending. b) Excellent flexibility of TCE during deformations. c) Tortuous pathways for charge transfer in thick MFE. d) Fast charge transfer in the porous structure of TCE. Reproduced from ref. [22].

2.4.1 Structure and Fabrication

As introduced before, traditional LBs are made by stacking metal-foil-supported electrodes (MFEs), in which active materials are coated onto the metal foils (Figure 2.16a). It is hard for the industrial roll-to-roll process to fabricate thick MFEs due to the easy delamination of the thick active material layer (Figure 2.16c). Hence, typical MFEs have a thickness of lower than 50 μm .¹²⁰⁻¹²² In contrast, textile composite electrodes (TCEs) are easier to be made with much larger thickness than MFEs, benefiting from the porous structure, which provides much space for active materials (Figure 2.16b). It can be realized by different kinds of strategies, including the coating method (e.g., dip-coating, blade-coating) (Figure 2.16d),^{51, 122-124} spinning method (e.g.,

electrospinning, dry spinning, and wet spinning) (Figure 2.16e),¹²⁵⁻¹²⁷ and in-situ growth method (e.g. hydrothermal reactions, electrodeposition) (Figure 2.16f).^{128, 129} Specifically, the infiltration of active material slurry into fabrics is supported by capillary force in fibrous substrate. For example, high-mass-loading LTO anodes (145 mg cm^{-2}) and LFP cathodes (168 mg cm^{-2}) were fabricated with the current collector of CNT-coated polyester textiles.¹²² By assembling this pair of TCEs into full cell, a high areal capacity of more than 20 mAh cm^{-2} was achieved. The fabrication process of the spinning method is somehow like the coating method but provides yarn-type electrodes that cannot be realized in MFEs. The in-situ growth of active material onto current collectors allows the fabrication of electrodes with complex structures, making it more available in structure design. In addition, improved interface adhesive between active materials and current collectors is realized by interfacial reactions without the usage of binder and (or) conductive agents.^{127, 130} The high proportion of active materials in the whole electrode implies a high energy density (or specific energy) of the battery.

2.4.2 Mechanical Property

Due to the intrinsic low yield strains of metal foils, MFEs are easy to crack and fracture after continuous bending cycles with a low radius of curvature (Figure 2.17a).^{131, 132} In addition, the interfacial adhesion between active materials slurry and metal foil is limited due to the flat surface of current collectors. It results in delamination of the active materials layer and finally breaks the pathways for electrons.¹³³ In contrast, TCE with fabric structure can efficiently dissipate the external stress and strain to maintain intact during deformations (Figure 2.17b). Besides, the large surface area of conductive

textiles offers a much better interface adhesive with active materials, preventing the delamination of the active materials layer.

Gao et al. proposed that soft textile current collectors can relieve the strain applied to the active material layer. The neutral surface shifts towards the active materials layer due to the lower Young's modulus of textile compared to metal foils. Not only the material but also the structure decide the modulus of the textiles. The relationships of Young's modulus between porous and solid structure can be expressed by:^{134, 135}

$$\frac{Y_p}{Y_s} = \left[\frac{2(1+\sqrt{2})^2}{15} \frac{5\pi+3(1-\rho)(1+\sqrt{2})^3}{25\pi+7(1-\rho)(1+\sqrt{2})^3} (1-\rho) \right] \quad \text{Equation 2.7}$$

Where ρ is the porosity, Y_p and Y_s represent Young's modulus of porous objective and solid objective with the same material. This equation indicates that the modulus of textiles with a porosity of 0.5 is only one-tenth that of solid ones. For the common textiles made of natural or synthetic polymer, which feature soft nature, fabric structure further improves the reliability in long-term usage. From another aspect, solid material can be fabricated into textiles for much better flexibility, such as glass fiber fabrics and carbon cloths. By reducing Young's modulus, not just the current collector itself becomes flexible but also the strain in the active material layer can be reduced.

2.4.3 Charge Transfer Kinetics

It is well-known that LBs store and convert energy by electrochemical reactions, which relates to several kinetic processes: a) solid-state diffusion of electrons and Li ions in active materials; b) charge transfer in the interface between electrode and electrolyte; c) diffusion of Li-ions in electrolyte and d) conduction of electrons in the external circuit.⁹⁰

The battery performance, especially the rate capability, is decided by the rate-limited step, which differs in diverse electrodes.

For the traditional MFEs used in commercial LIBs, the charge transfer kinetics largely depends on the thickness of the active materials layer (Figure 2.17c). In general, active material has lower electrical conductivity than the current collector and lower ion conductivity than the electrolyte. Hence, the thick active material layer will cause sluggish electrochemical kinetics, thus leading to poor rate performance of the battery. On the contrary, TCEs exhibit much faster transportation of electrons and Li-ions, benefiting from their large surface area (Figure 2.17d).¹³⁶⁻¹³⁸ Better infiltration property of TCEs makes more active materials directly exposed to the electrolyte, shortening the diffusion length of Li-ions. In addition, a large contact area between active materials and current collectors provides better conduction of electrons by reducing the localized current. This advantage on charge transfer kinetics endows TCEs with enhanced rate performance and long-term stability. For instance, a TCE made of Ni-coated cotton fabric and hollow V_2O_5 has a high specific capacity of 222.4 mAh g^{-1} at a current density of 200 mA g^{-1} .¹³⁹ However, the contrast sample, a MFE with same active material only showed specific capacity of 102 mAh g^{-1} . In the meantime, Ni-cotton/ V_2O_5 electrode presents stable capacity exertion in 500 cycles, much longer than that of Al/ V_2O_5 electrode.

2.4.4 Application of TCEs in FLBs

TCEs are usually made by coating suitable metal layers onto the textiles as the metal has high conductivity. In view of the electrochemical stability, Lee et al. fabricated Ni-

coated polyester textile current collectors and made the TCEs by blade-coating LFP and LTO onto them.⁵⁵ The resultant LIBs using TCEs could work with fluctuation of potential during the folding process, but the foil-based one stopped after several cycles of folding. Subsequently, another work from them studied the influence of the weaving structure of textiles on battery performance.¹⁴⁰ They found that the nonwoven TCEs have better tolerance after bending and enhanced cyclic capacity than those of woven TCEs. It was explained by the suitable structure of nonwoven that allows higher electric conductivity and more compact packing of active materials. Except for the construction of the substrate, the morphology of the metal layer also affects the performance of textile-based LIBs. By precise control of electroplating after the electrodeless deposition (ELD) process, Ni and Cu nano-reliefs formed on the surface of cotton fabrics.¹⁴¹ Compared to the conductive textiles made by the ELD method, the contact area between active materials and current collectors was enhanced. Thus, the elevated transport of electrons led to a significantly improved rate performance.

Textile structures are also proven efficient in controlling the morphology of Li deposition in Li metal batteries (LMBs). Li incorporated polyethylene terephthalate (PET) nonwoven was fabricated by electrochemical deposition method, and it showed reliable flexibility under rolling deformation (Figure 2.18a).¹⁴² In addition, the conductive fibrous skeletons (CFS)-Li showed better cyclic stability than the control Cu-Li sample without obvious increase in overpotential (Figure 2.18b). They demonstrated that CFS-Li efficiently acted as a three-dimensional host for the accommodation of Li metal, thus preventing the random growth of Li dendrites. As a result, uniform plating/stripping processes were achieved in TCEs.

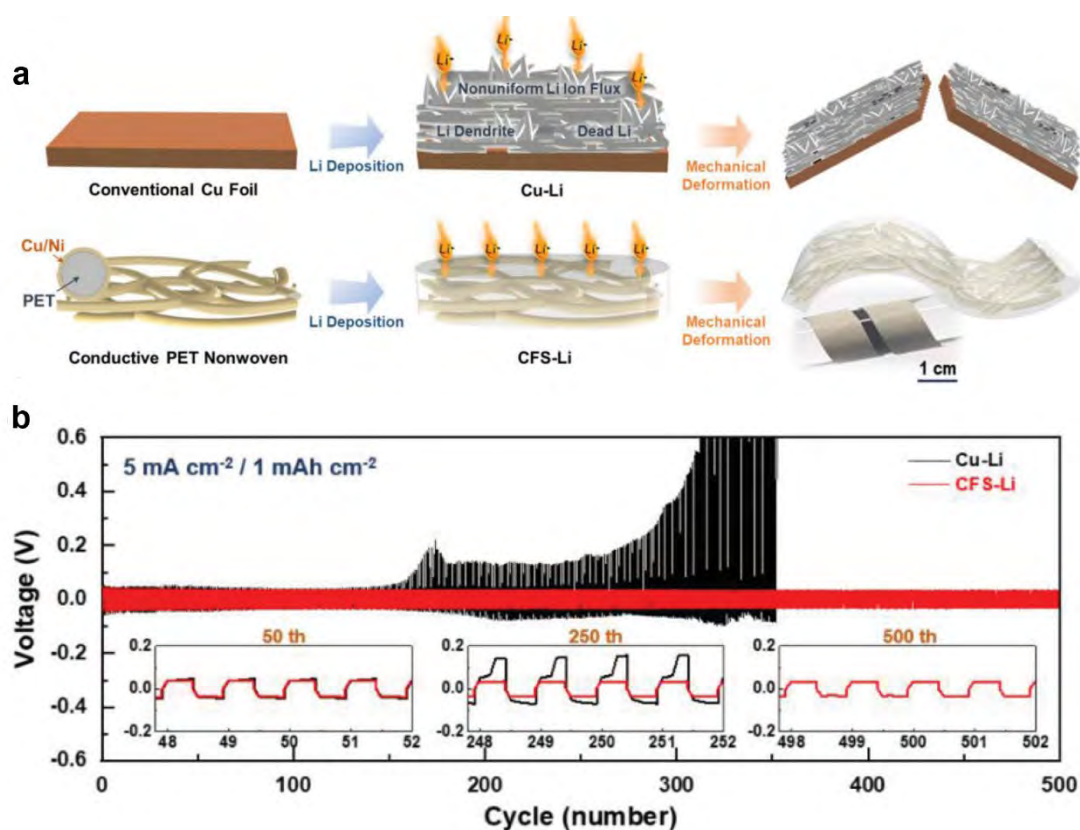


Figure 2.18. a) Schematic representation depicting a better deformability of CFS–Li compared to Cu–Li. b) Galvanostatic plating/stripping profiles of Cu–Li and CFS–Li electrode with counter electrodes of Li foils. Reproduced from ref. [142].

Besides the LIBs and LMBs, TCEs can be applied to other battery systems. Our group reported a full-textile-based Li-S battery using Ni and Cu-coated carbon cloth as current collectors for the cathode and anode (Figure 2.19a and 2.19b). Due to the advantages summarized above, the Li-S full cells exhibit high capacity retention of $\sim 99.9\%$ per cycle at different mass loadings (Figure 2.19c).⁵⁶ The fabric electrodes are mechanically reliable during bending cycles, even under a low radius of curvature (5 mm). Hence, the resultant Li-S full cell work normally in a bending state, only with a bit of lower capacity exertion (Figure 2.19d).

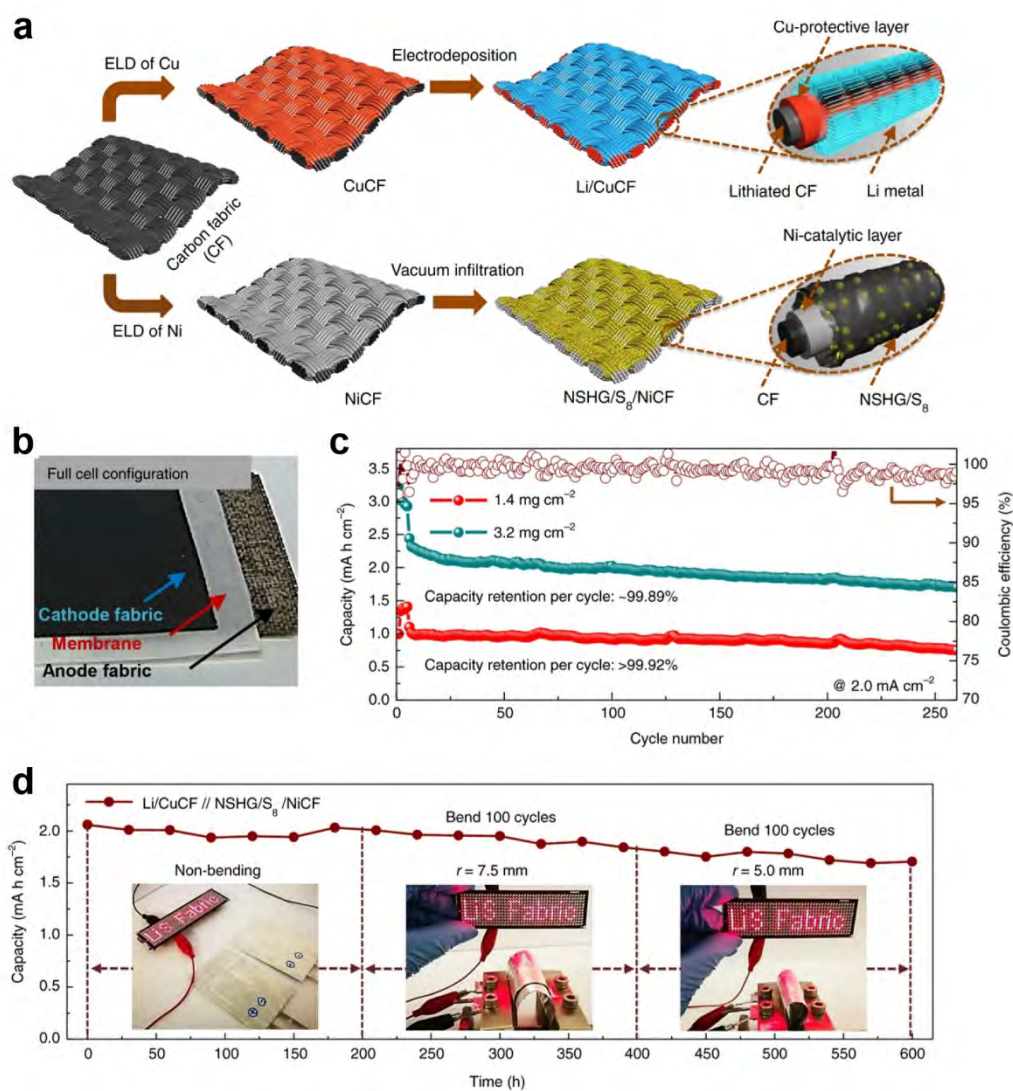


Figure 2.19. a) Schematic fabrication process and structure of carbon fabric-based electrodes. b) Images for cell configuration of Li-S battery. c) Cycle performance of Li-S full cell with different mass loadings. d) Cycle performance of pouch cell under different bending states. Insets illustrate that the flexible Li-S battery can still work normally in a bending state. Reproduced from ref. [56].

2.4.5 Challenges for TCEs-based FLBs

Despite TCEs show many advantages in fabricating FLBs, they still need to improve on some issues, mainly the relatively high resistance of textile-based current collectors and the low energy density of resultant FLBs.

2.4.5.1 Relatively High Resistance of Textile-based Current Collectors

Compared to metal foils, conductive textiles usually show higher resistance because of their intrinsic low conductivity and porous structure. For instance, CNT-based fabrics have high resistance of $1\ \Omega\ \text{sq}^{-1}$, about three orders higher than 10- μm Cu foil ($1.6 \times 10^{-3}\ \Omega\ \text{sq}^{-1}$).¹⁴³ Such relatively high resistance may have a tiny influence on battery performance in laboratory fabrication because of the small battery size. However, the negative effect will be enlarged with the increase in the battery size, leading to a high potential and energy loss.¹⁴⁴ By comparison, metal-coated textiles presented lower conductivity due to the highly conductive nature of metal. A conformal metal layer with robust adhesion to the substrate can be realized by the PAMD method.^{23, 145, 146} In this process, an ultrathin polymer layer is first grafted onto the fabrics, acting as a bridge between the substrate and metal layer. As the metal is reduced under the catalyst tethered by polymer chains through electrostatic attraction, the resultant conductive textiles are highly conductive and mechanically durable. The conductivity of the resultant textile is decided by the metal plating thickness and is easily controlled below $0.1\ \Omega\ \text{sq}^{-1}$.

2.4.5.2 Low Energy Density of TCEs-based FLBs

TCEs-based FLBs show comparatively low volumetric or gravimetric energy densities to commercial rigid batteries. It is attributed to the low packing density of active

materials for porous fabrics in which the space cannot be fully filled. The chosen fabrics in most reported works are usually thick with hundreds of micrometers, indicating a large portion of inactive space and weight. As discussed before, conductive textiles are fabricated by incorporating conductive materials and fabrics through different methods. Because most fabrics are intrinsically insulative, the conductivity of the textile-based current collector largely depends on the mass of the conductive part. Hence, it refers to a tradeoff between the electric conductivity of the current collector and the gravimetric energy density of the battery. It requires more effort into optimization on properties of conductive textiles, especially a combination performance.

2.5 Pathways for Improvements in Energy Density

Energy density is the most important parameter, which is decided by the output power and the battery's weight (or the volume). Hence, the development of the energy-dense LIB focuses on squeezing the performances of active materials in the cathode (Li-rich¹⁴⁷⁻¹⁴⁹ or high-voltage materials¹⁵⁰⁻¹⁵²) and the anode (Si¹⁵³⁻¹⁵⁵ or Li metal¹⁵⁶⁻¹⁵⁸). Another pathway aims to decrease the denominator, i.e., the weight or volume composed of active and inert parts. A direct method to improve the energy density is to enhance the ratio of active materials in the electrode, which can be realized by increasing the mass loading of active materials or decreasing the weight of current collectors. As this thesis is focused on the current collector rather than the material so explorations on new active materials are not covered in this chapter. Here, only the specific discussion of the high-mass-loading electrodes and lighter current collectors is illustrated.

2.5.1 High-mass-loading Electrode for Improved Energy Density

For a typical electrode, there are many inactive components including the binder, the conductive agent and the current collector. With the development of the slurry preparing techniques, the proportions of active material have reached the limit of 92-95 wt%. Therefore, researchers tried to fabricate thick electrodes with as possible as more active materials on the current collector. However, poor rate and cyclic performance are always obtained in thick electrodes due to the limited electrochemical kinetics. For conventional electrodes, random but close packing of active materials, conducting agent and binder generates a porous structure with high tortuosity (Figure 2.20a).¹²¹ It is clear that the diffusion length of the Li ions quickly rises with the increased thickness, leading to a slow charge transfer process. Hence, developing novel electrode structures with low tortuosity is urgently required for improving the electrochemical kinetics of thick electrodes.

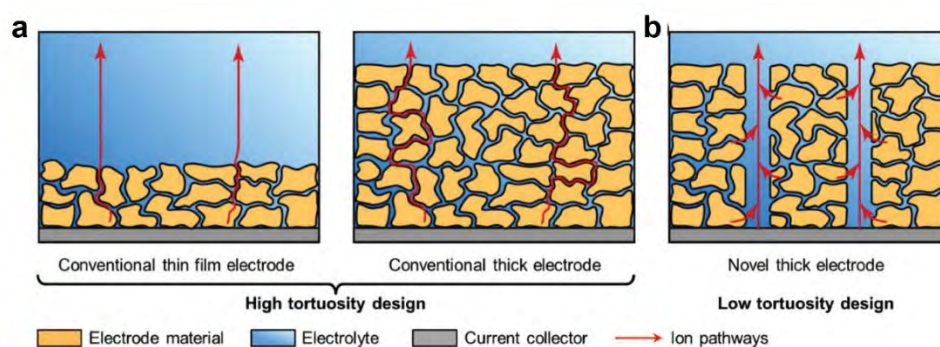


Figure 2.20 Schematic illustration of ion pathways in different electrodes with a) high tortuosity and b) low tortuosity. Reproduced from ref. [121].

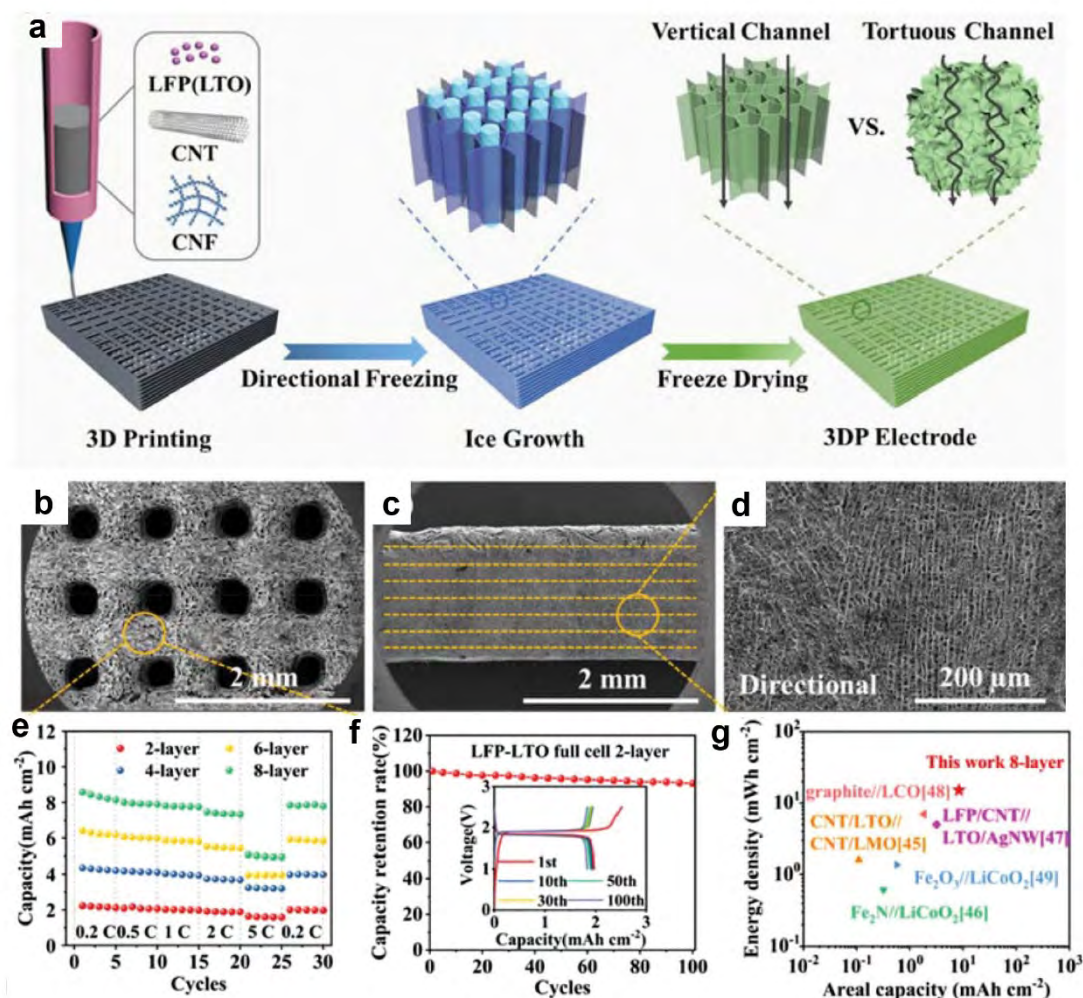


Figure 2.21 a) Schematic fabrication process of 3D printed FLB electrode. The b) top, c) side view, and d) enlarged SEM images of directional freezing printed LFP/CNT/CNF electrode. e) Rate performance of the full cells with different layered structure. f) Cycle performance of a full cell with 2-layered structure at 1 C. g) Comparison of areal capacity and energy density between the 8-layered FLB with representative FLBs. Reproduced from ref. [159].

A well-designed structure with vertical channels was prepared by 3D printing and subsequent directional freezing method (Figure 2.21a).¹⁵⁹ CNF was added as the rheology conditioner to monitor the rheology property of the ink while CNT provided a 3D conductive network with fast conduction of electrons. Assisted with the ice growth,

the prepared electrodes presented a uniform lattice structure with directional pores that penetrated the entire electrodes from bottom to top (Figure 2.21b-d). Thanks to the low-tortuosity design, the 8-layer electrodes showed a high capacity of 8.4 mAh cm^{-2} at 0.2 C and an outstanding capacity retention of 59.1% from 0.2-5 C (Figure 2.21e). The 2-layer electrode exhibited reasonable cyclic stability, with 93.1% after 100 cycles. Compared to other FLBs, it demonstrated much higher energy density because an improved active materials ratio in electrodes was achieved without significant deterioration of the electrochemical performance. Other anisotropic structures are also manufactured by using the magnetic field,^{160, 161} template method,¹⁶²⁻¹⁶⁵ extrusion-type 3D printing or direct ink writing.¹⁶⁶⁻¹⁷²

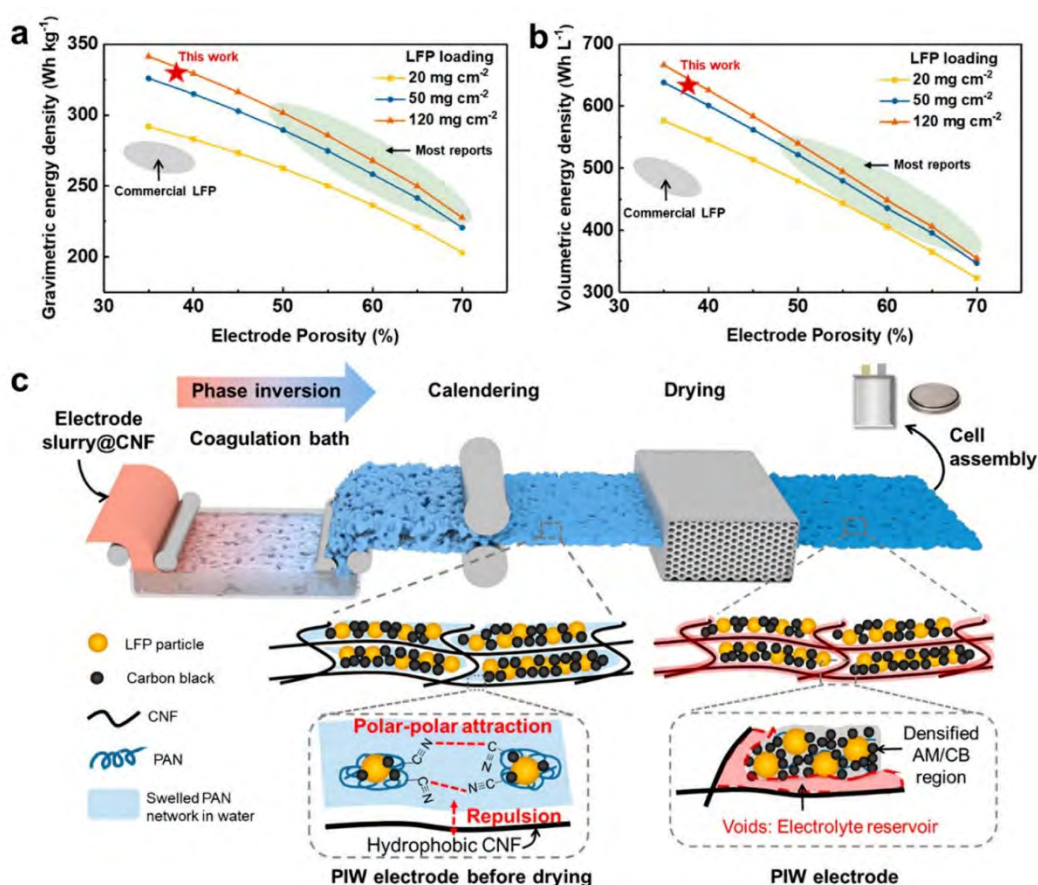


Figure 2.22 Predicted relationship between porosity and a) gravimetric and b) volumetric energy density. c) Schematic fabrication process of the PIW electrode. Reproduced from ref. [173].

Apart from the unique structure design for electrodes, Wu et al.¹⁷³ proposed a facile but efficient way to manufacture the thick electrode. The relationships between the porosity and gravimetric and volumetric energy density indicate that a high energy density is achieved in a low porosity (Figure 2.22a and 2.22b). However, low porosity always leads to low infiltration ability of the electrolyte and thus inferior electrochemical performances. In this work, a densified active material region, a conductive CNF region, and a void region in between are created by using phase inversion and wet calendaring method (Figure 2.22c). The microvoids that dispersed adjacent to the active material facilitated the diffusion of ions within the compact electrode by loading much electrolyte. Therefore, a thick electrode with 65 mg cm^{-2} loading of LFP still displayed satisfied rate and cycle performances, much better than the conventional thick electrodes. Even, the mass loading was further increased to 126 mg cm^{-2} , the electrode exhibited a high areal capacity of 21.4 mAh cm^{-2} at 0.05 C and 8.1 mAh cm^{-2} at 0.5 C .

2.5.2 Light (or Thin) Current Collector for Improved Energy Density

An alternative way is cutting the weight (or thickness) of the current collectors. In commercial LIBs, the current collectors used for the anode and the cathode are Cu and Al foils. In 1999, the thicknesses of Cu and Al foils were $20 \text{ }\mu\text{m}$ and $18 \text{ }\mu\text{m}$, accounting for $\sim 19 \text{ wt}\%$ and $\sim 6 \text{ wt}\%$ of the whole battery (Figure 2.23).¹⁷⁴ In the past twenty years, the thicknesses of metal foils quickly drop to $6 \text{ }\mu\text{m}$ for Cu and $10 \text{ }\mu\text{m}$ for Al, leading to a much lower weight ratio of the battery.¹⁷⁵⁻¹⁷⁷ Such decreases in thickness and weight of current collectors are pretty meaningful to the battery. Choudhury et al. presented the influence of light current collectors by using Li/high Ni-oxide system as an example (Figure 2.23b).¹⁴⁴ If the well-matured technology ($\text{Cu/Al} = 8/12 \text{ }\mu\text{m}$) is used, the specific energy of the cell level is only $\sim 360 \text{ Wh L}^{-1}$. With the decrease in thicknesses

of Cu and Al foils, the specific energy increases to 384 and 394 Wh L⁻¹, about 6.7% and 9.4% higher than well-matured ones. It should be noted that the improvement in specific energy of LIBs is only ~5% per year.

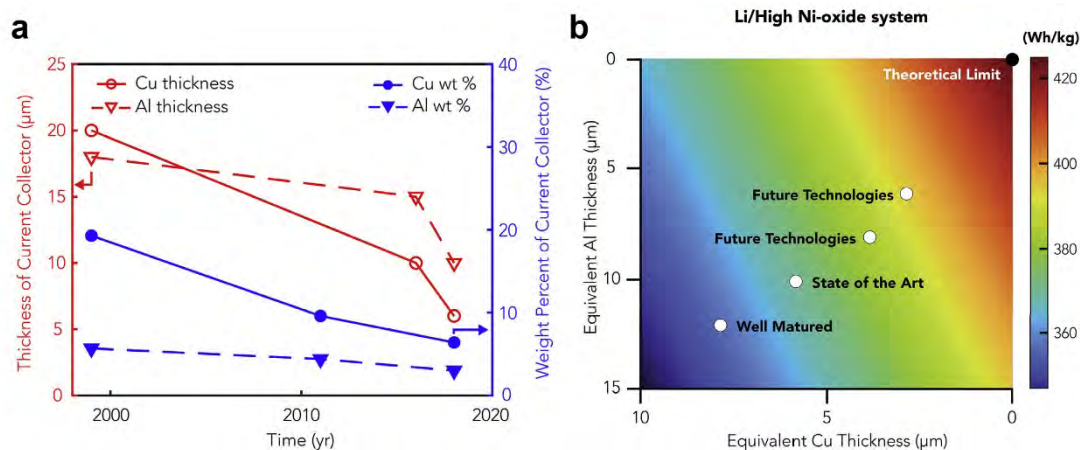


Figure 2.23 a) Thickness and weight ratio of Cu and foils in the last twenty years. b) A 2D colormap showing the improved specific energy by making the current collectors lighter. Reproduced from ref. [144].

Apart from making foils thinner, porous foils and metal-on-plastic foils are two main methods that lighten the current collectors. A 1.5- μm thick, porous Cu foil was prepared by compressing Cu nanowires together (Figure 2.24a and 2.24b).¹⁷⁸ It showed much lower areal density and better interfacial adhesion between the current collector and active materials than Cu foil-based electrode. However, the fabrication process is relatively complex and the cost is high. Porous foils can be fabricated by creating micro holes via laser, and the removed area accounted for ~ 20% of the original area (Figure 2.24c and 2.24d).¹⁷⁹

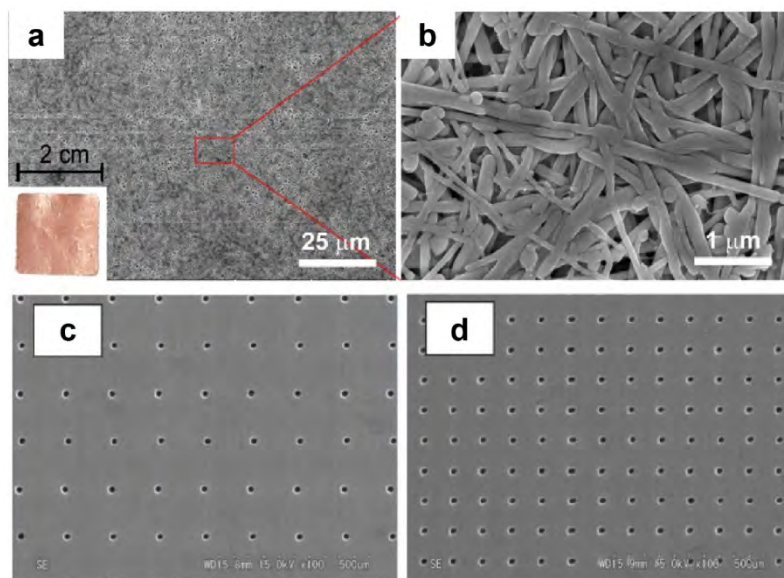


Figure 2.24 Morphology of a and b) Cu nanowires formed current collector, reproduced from ref. [178]. c and d) Cu foil with holes created by the laser, reproduced from ref. [179].

Another route is replacing metal foils with metal-coated plastic current collectors, whose properties including conductivity and areal density could be easily tuned. In 2020, Cui et al. reported a polyimide (PI)-based current collector coated by Al or Cu by sputtering technology (Figure 2.25a).²⁰ Compared to the high areal density of $\sim 8 \text{ mg cm}^{-2}$ for $9 \text{ }\mu\text{m}$ -thick Cu foils, this plastic foil shows a much lower specific mass of $\sim 2 \text{ mg cm}^{-2}$ (Figure 2.25b). The full cell using PI-based current collectors exhibited comparable cyclic performance to traditional batteries using metal foils, demonstrating that the PI substrate had been fully separated by a metal coating layer (Figure 2.25c). Benefiting from the lower areal density, LIBs using PI-based current collectors presented an improvement of $\sim 15\text{-}25\%$ in specific energy than conventional ones (Figure 2.25d). In addition, the metal-on-plastic method allows facile functionalization of the substrate. A fire retardant, polyimide-triphenyl phosphate (TPP) was incorporated into the PI substrate and the resultant electrode has excellent flame retardancy.

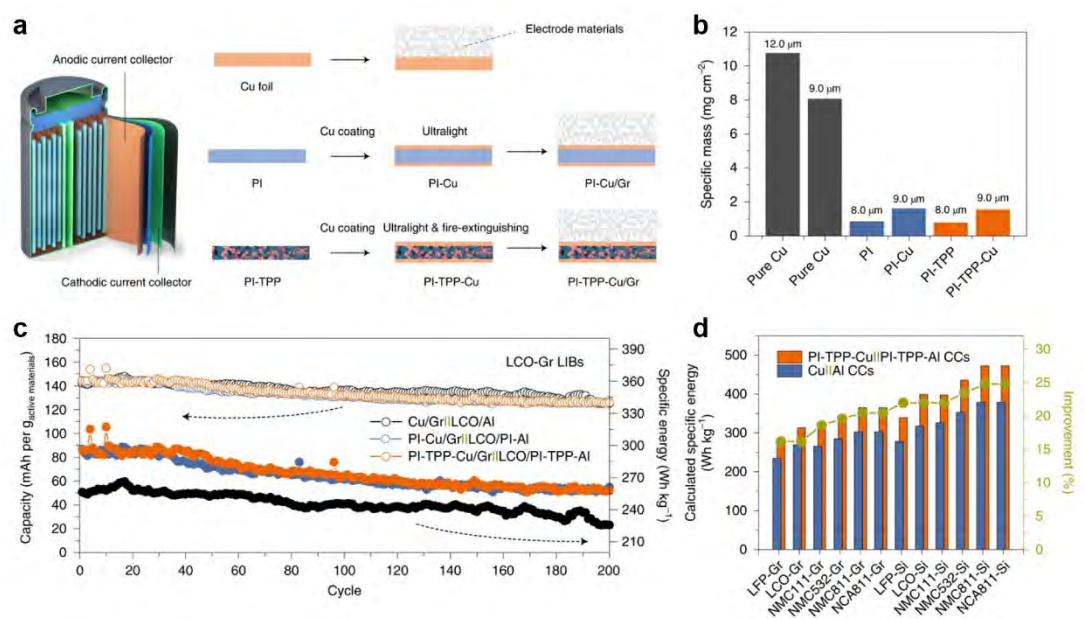


Figure 2.25 a) Schematic fabrication process of PI-TPP current collectors. b) Specific mass of Cu foil and PI-based current collectors. c) Cycle performance of full cell using PI-TPP-based current collectors. d) Calculated specific energy of different LIBs using commercial current collectors and PI-based current collectors. Reproduced from ref. [20].

Chapter 3. Methodology

In this chapter, the general methodology is introduced. It includes the fabrication and protection methods of the fabric-based current collectors, assembly of the coin cell and pouch cell, characterizations of the electrical, mechanical, and electrochemical performances, and flexibility tests for the textile-based Li-ion batteries (LIBs).

3.1 Materials

All the chemicals are purchased from commercial companies and listed as follow: Ethyl Alcohol (EtOH, 99.9%, AQA), acetic acid (100%, Acros), 3-(trimethoxysilyl)propyl methacrylate (MPTS, 98%, Sigma-Aldrich), [2-methacryloyloxy)ethyl]trimethylammonium chloride solution (METAC, 80 wt %, Sigma-Aldrich), potassium persulfate (KPS, 99.5%, Uni-Chem), ammonium tetrachloropalladate(II) (Pb 37%, Alfa Aesar), Nickel (II) Sulfate (AR, Uni-Chem), tri-Sodium citrate dihydrate (99.5%, Fisher Chemicals), Lactic acid (90%, Acros), ammonium hydroxide (25%, VWR Chemicals), dimethylamine borane (DMAB, 98%, J&K), sodium acetate (VWR Chemicals), sodium hypophosphite (AR, Aladdin), copper(II) sulfate pentahydrate (99.0%, Uni-Chem), potassium sodium tartrate tetrahydrate (99.5%, Sigma-Aldrich), sodium hydroxide (97%, Uni-Chem), formaldehyde solution (37% - 41%, BDH), commercial copper plating solution (Plug N Plate Cu solution, Caswell Inc., USA), graphite (Gr, MA-EN-AN-03010F, Carnd), lithium nickel cobalt manganese oxides (NCM811, MA-EN-CA-0B0307, Carnd), lithium iron phosphate (LFP, MA-EN-CA-05, Carnd), lithium cobalt oxide (LCO, MA-EN-CA-0Q, Carnd), carbon black (Super-P, MA-EN-CO-01, Carnd), polyvinylidene fluoride (PVDF, 5130, Solvay), 1-Methyl-2-pyrrolidinone (NMP, Aladdin),

3.2 Preparation of metal-coated fabrics (MFs)

This research focuses on the advance of current collectors so other components of batteries are the same as those of commercial ones. Superlight and ultrathin glass fiber (GF) and polyethylene terephthalate (PET) fabrics were chosen as flexible substrates. Cu and Ni (or the Ni/P composite) were coated onto these fabrics by the polymer-assisted metal deposition method (PAMD). Based on the chemical and electrochemical stability, Cu-coated and Ni (or Ni/P) coated fabrics were used as current collectors for the anode and cathode, respectively.

3.2.1 Preparation of Textile-based Current Collectors

3.2.1.1 *Pre-treatment of Fabrics*

At first, fabrics were treated with plasma for 30 mins. Then, fabrics were soaked in a solution for 1 hour, which contains EtOH, acetic acid, deionized (D.I.) water, and MPTS with a volume ratio of 95:1:4:4. The carbon-carbon double bonds on the surface of treated fabrics provide sites for the polymerization of METAC, which can interact with the Pd^{2+} catalyst. The polymerization was conducted in a METAC solution (20% v/v in water) at 80 °C for 3 hours, by using potassium persulfate (2 g L^{-1}) as initiator. At last, polymerized METAC-coated fabrics were dipped into a $(\text{NH}_4)_2\text{PdCl}_4$ solution (5 mM) for 30-60 min.

3.2.1.2 *Electroless Deposition (ELD) of Cu*

The fabrics loaded with catalyst were then immersed into the ELD bath. It was realized by adding the reducing solution (HCHO , 36 mL L^{-1}) into the Cu^{2+} source solution

containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (13 g L^{-1}), NaOH (12 g L^{-1}), and $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (29 g L^{-1}). The ELD time is 30-60 min, depending on the target conductivity and areal density.

3.2.1.3 ELD of Ni

Similar to the ELD process of Cu. ELD bath of Ni was conducted by adding the reducing solution of DMAB (0.75 g L^{-1}) into the Ni^{2+} source solution containing $\text{Ni}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (100 g L^{-1}), sodium citrate (50 g L^{-1}), lactic acid (25 g L^{-1}) at the pH of ~ 7.5 (regulated by ammonium hydroxide). The ELD time is 60-90 min, depending on the target conductivity and areal density.

3.2.1.4 ELD of Ni/P Composite

ELD of Ni/P composite was carried out by changing the reducing agent and Ni^{2+} sources solution of the ELD bath. The source solution consists of $\text{Ni}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (40 g L^{-1}), sodium citrate (24 g L^{-1}), and sodium acetate (24 g L^{-1}) in DI water. The pH was regulated to ~ 4 by lactic acid. The ELD bath was obtained by adding the sodium hypophosphite solution (24 g L^{-1}) into the source solution. The ELD process was conducted at 85°C for 60-90 min, depending on the target conductivity and areal density.

3.2.2 Protection of Textile-based Current Collectors

3.2.2.1 Additional Electroplating of Cu after ELD

The electrodeposition was carried out using CuPET as the working electrode and Cu foil as the counter electrode at a constant current density of 0.5 mA cm^{-2} with different plating time.

3.2.2.2 Atomic Layer Deposition (ALD) Method

The ALD method was utilized to protect the current collectors or electrodes by depositing several-nanometer-thick Al_2O_3 . ALD was conducted at 80 °C in a thermal ALD system (Savannah, Veeco), and the deposition thickness of every cycle in this condition is 0.75 Å.

3.2.3 Preparation of Textile-based Electrodes

In this work, commercially used active materials, including Gr for anode, NCM, LCO, and LFP for cathode were adopted to test the performances of textile-based current collectors. The active materials were mixed with super P and PVDF with a weight ratio of 8:1:1 in a certain amount of NMP. Then the slurry was blade-coated onto the metal foils or conductive fabrics. The samples were dried at 80 °C, punched, compressed, and thoroughly dried under vacuum at 110 °C.

3.2.4 Cell Assembly

3.2.4.1 Assembly of Coin Cell

Coin-type cells (CR2032) were assembled in an Ar-filled glovebox. For the half-cell tests, Gr, NCM, LCO, and LFP electrodes were the working electrodes, and the counter electrodes were Li foils. Separator Celgard 2325 and commercial electrolyte of LBC3401A4 (CAPCHEM, LiPF_6 in EC/DEC solvent, and FEC as an additive) were used in all the cells. For the full cell, the Gr electrode was initially activated and matched with cathodes. The N/P ratio was controlled in the range of 1.1-1.2. The specific assembly process is described as follows. At first, the cathode was put onto the bottom case (cathode case), and 50-80 μL electrolyte was added to wet the electrodes.

By covering a piece of separator, the anode was placed on it, aiming at the cathode electrode. A piece of 1.5 mm stainless steel and a hollow-shaped spring was put on the electrode, followed by the upper case (anode case) sealing.

3.2.4.2 Assembly of Pouch Cell

Unlike the coin-type cases, pouch cells were fabricated by sealing the electrodes into Al laminated composite film at Ar atmosphere. The cathode and the anode were cut into a rectangular shape (the anode is a little bit larger than the cathode) and were welded with Al tab and Ni tab, respectively. The separator was sandwiched between the cathode and the anode, followed by dropping a certain amount of electrolyte (based on the capacity). Finally, the pouch cell was sealed by the MSK-115A machine with the Al laminated composite film.

3.3 Characterizations

3.3.1 Morphology characterization

Morphology observation was conducted in a scanning electron microscope (SEM, Tescan, VEGA3) and a field-emission scanning electron microscopy (FESEM, Tescan, MAIA3). Elemental analysis was examined by the Oxford energy dispersive X-ray (EDX) spectroscopy system. All the samples are fixed on the specific stage by conductive tape, followed by the deposition of Au.

3.3.2 Mechanical test

Mechanical performances of current collectors were tested by a universal testing machine (Instron 5566, USA) at a cross speed of 50 mm min⁻¹ and a gauge length of 20 mm. All the samples are cut into rectangle-shape with a size of 40 mm × 10 mm.

3.3.3 Conductivity test

The electrical properties of current collectors were characterized by a source meter (Keithley 2400, USA) with a four-point test probe (HPS58003, Helpass, China). During the bending process, real-time conductivities of current collectors and electrodes were also monitored. The bending process was conducted on a homemade motion apparatus.

3.3.4 Electrochemical tests

Battery performances were obtained by a battery test system (BTS 3000, Neware, China). Electrochemical impedance spectroscopy (EIS), liner scanning voltammetry (LSV), and cyclic voltammetry (CV) were carried out by using an electrochemical workstation (Biologic, France).

3.3.5 Fourier Transform Infrared Spectroscopy (FTIR) Characterization

FTIR spectra were recorded by PerkinElmer FT-IR Spectrum 100 equipped with an attenuated total reflection (ATR) accessory. The scanning range is set to 4000 cm^{-1} to 650 cm^{-1} , and the resolution is 1 cm^{-1} . After charge-discharge cycles, the Cu-coated fabrics were etched in FeCl_3 solution to remove the Cu. These samples were thoroughly washed and dried before tests.

3.3.6 X-ray Photoelectron Spectroscopy (XPS) Analysis

XPS analysis was carried out using an XPS system (Thermo Fisher Nexsa, USA). After charge-discharge cycles, the coin cells were disassembled. The electrodes and separator were washed with ethylene carbonate/diethyl carbonate (1:1, v/v) solution to remove the Li salts before XPS tests.

Chapter 4. Improved Energy Density by using Super-lightweight Metallic Glass-fiber Fabrics

In this chapter, we develop a new type of superlight and electrochemically stable metallic current collector, glass-fiber fabrics (MGFs). It is well known that GF is widely used as a low-cost and stable insulating material. The MGF-based electrodes display excellent mechanical properties and flexibility after 100,000 bending cycles by fully exerting these merits. Simultaneously, a sharp cutting on the weight of the current collector is realized that these MGFs only weigh 2.9-3.2 mg cm⁻², 61% and 24% lighter than the commonly used Cu and Al foil. By replacing the metal foils with MGFs, the energy density can be improved by 9-18% for different kinds of active materials without any deterioration of the cyclic stability. Moreover, the MGF-based pouch cell is highly flexible that can work normally after thousands of bending at a low bending radius of curvature (2 mm).

4.1 Introduction

The rapid development of portable and wearable electronics put forward an urgent demand for high-energy storage systems.¹⁸⁰⁻¹⁸² As an essential member, Li-ion batteries (LIBs) show typical energy densities of 150~210 Wh kg⁻¹,^{10, 183-185} which almost reach the theoretical limit if using the commonly used components. Researchers have taken much effort into the development of new active materials and battery chemistries.¹⁸⁶⁻¹⁸⁹ These ongoing studies, however, require quite a long time to reach the commercialization level. As an alternative pathway, reducing the mass ratio of the

inactive materials in the battery can directly increase the energy density. The most effective approach is to cut the weight of the current collectors because they account for 15~35 wt% of the whole battery.^{177, 190} Taking the commonly used Cu foil (7.5 mg cm⁻²) and Al foil (4.2 mg cm⁻²) for example, reducing 50% weight of these metal foils can create a 10~15% rise in energy density. However, it is hard to largely cut the weight of these metal foils in view of the mechanical strength, conductivity, and processing ability.

Recently, there are a number of works replacing metal foils with other soft and lightweight materials. By merit of low mass density and good flexibility, carbonaceous materials such as carbon nanotube (CNT) films,^{51, 191, 192} graphene foams,^{53, 193} and carbon cloth^{56, 194} were widely reported. In addition, polymer-based current collectors including metal-coated polymers,^{195, 196} and conducting polymers^{20, 197} are also developed. Although some works propose improved energy density, the complex preparation and high cost seriously impede the scale-up fabrication for the LIBs industry.

Herein, we report the development of a new type of superlight, highly conductive electrochemically stable, and fire-retardant current collector: metallic glass fiber fabrics (MGFs). The superiority of MGFs is realized based on two aspects: 1. glass fiber has many advantages, such as high mechanical strength, chemical stability and fire retardance; 2. the polymer-assisted metal deposition (PAMD) method ensures uniform and mechanically robust metal coatings. With the much decreased areal density of MGFs compared to the Cu and Al foils, the batteries using MGFs present improved energy density. In the meantime, the batteries also display high flexibility thanks to the

good deformability of MGFs.

4.2 Experimental Part

4.2.1 Preparation of Metal-coated Glass Fiber Fabrics (MGFs)

MGFs were obtained by depositing Cu or Ni onto the GFs through the PAMD method.

Detailed preparations can be found in **Chapter 3.2.1**.

4.2.2 Cell Assembly

The preparation details of electrodes and cell assembly can be found in **Chapter 3.2.3 and 3.2.4**, respectively.

4.2.3 Characterization

Morphology observations were conducted in a Scanning Electron Microscope (SEM, Tescan VEGA3). Mechanical performances of current collectors were tested by a universal testing machine (Instron 5566, USA). The electrical properties of current collectors are characterized by a source meter (Keithley 2400, USA). Battery performances were obtained by a battery test system (BTS 3000, Neware, China). Linear scanning voltammetry (LSV) and cyclic voltammetry (CV) were carried out by using an electrochemical workstation (Biologic, France). Detailed information can be referred to **Chapter 3**.

4.3 Results and Discussion

4.3.1 Fabrication of MGFs and Basic Performances

The fabrication processes of MGFs and MGF-based flexible batteries are illustrated in Figure 4.1. Superlight commercial GFs with an areal density of 2 mg cm^{-2} were chosen as the substrate then Cu and Ni were deposited onto fabrics to obtain the Cu-coated GFs (CuGFs) and Ni-coated GFs (NiGFs). As well known, GFs are widely used as a kind of protection material because of their outstanding environmental stability and mechanical performance, which are also important merits for current collectors.

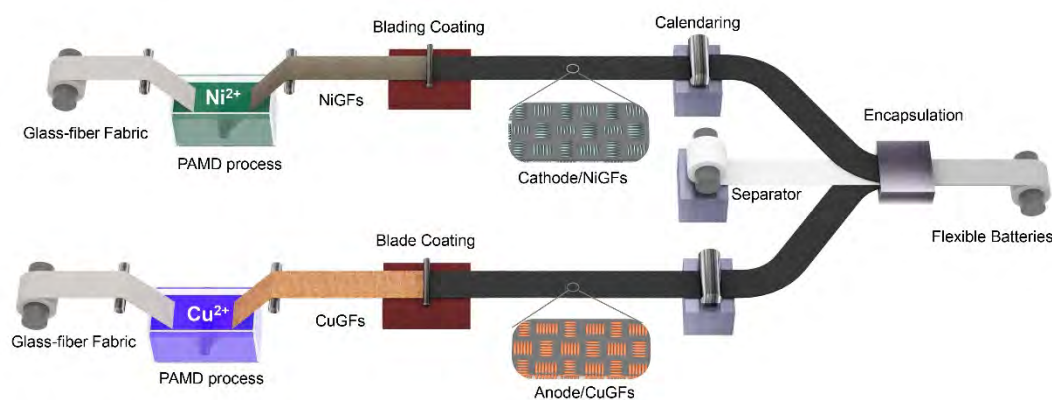


Figure 4.1 Schematic fabrication of MGFs and textile-based flexible batteries.

After the PAMD process, CuGF and NiGF maintain their original structure of plain weave (Figure 4.2). Cu and Ni are uniformly coated onto every single fiber without obvious defects. The polymer interlayer acts as a buffer layer and also a bonding layer between the fabrics and the coated metal layer. Such a good interfacial adhesion ensures the long-term reliability of the metal coating.

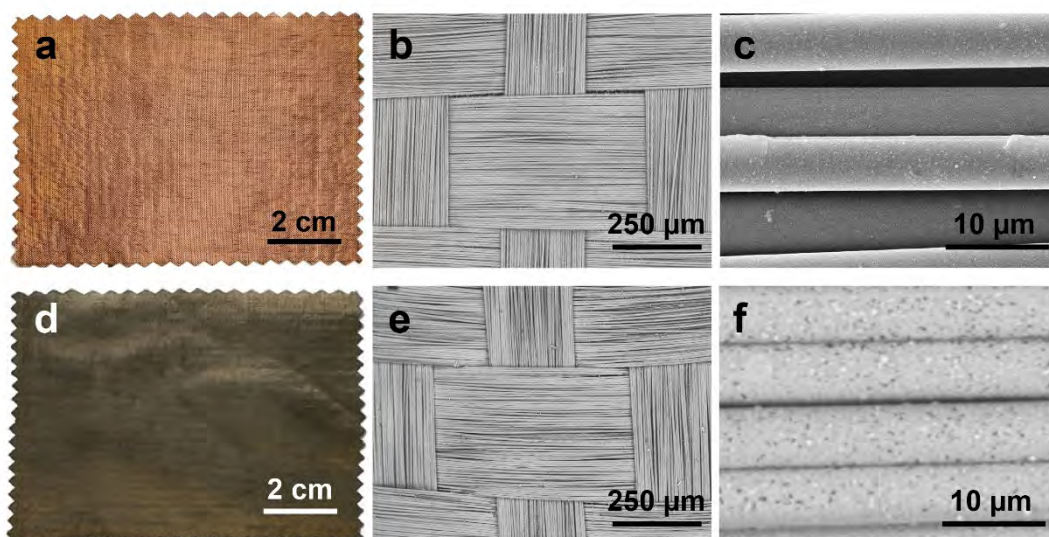


Figure 4.2 a) Optical image and b, c) SEM images of CuGF; d) Optical image and e, f) SEM images of NiGF.

Conductivity is a vital merit for current collectors as their most important function is the transportation of electrons. A high conductivity of MGF means a high metal loading which will cause an increase in the weight of the current collector and thus a decrease in specific energy. The ELD processes of Cu and Ni start from the nucleation of metal nanoparticles (Figure 4.3a and e). At this stage, the conductivities of resultant fabrics are very low as there are only a few conductive pathways within fabrics (Figure 4.4). With the extension of the ELD time, these nanoparticles are connected to each other and finally form a continuous metal layer (Figure 3). As a result, the conductivity of the fabrics increases a lot when the metal loadings are higher than $\sim 0.7 \text{ mg cm}^{-2}$. To balance the conductivity and areal density, the final areal density of CuGF and NiGF are 2.9 mg cm^{-2} and 3.2 mg cm^{-2} .

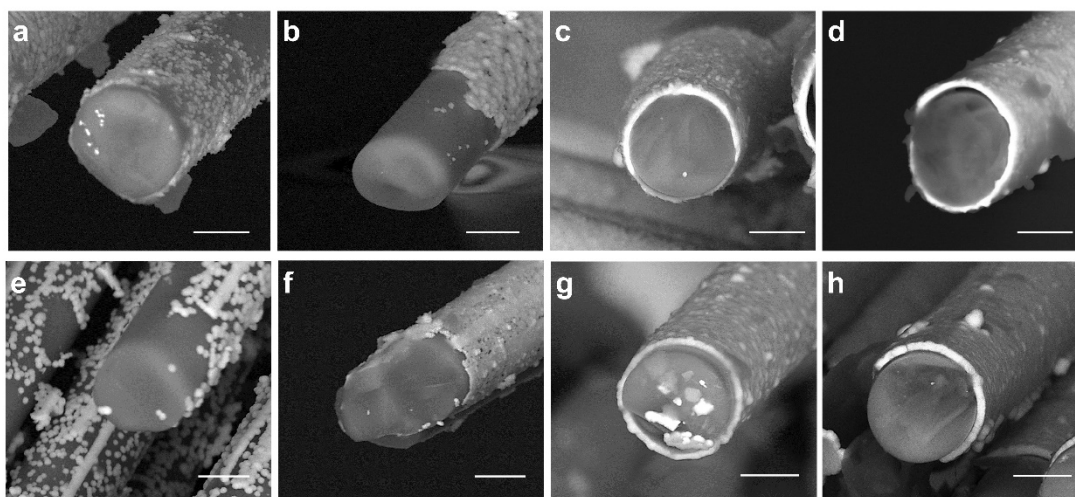


Figure 4.3 SEM images of CuGF with Cu loading of a) 0.45 mg cm^{-2} , b) 0.70 mg cm^{-2} , c) 0.84 mg cm^{-2} and d) 0.92 mg cm^{-2} . SEM images of NiGF with Ni loading of e) 0.42 mg cm^{-2} , f) 0.75 mg cm^{-2} , g) 1.03 mg cm^{-2} and h) 1.22 mg cm^{-2} . The scale bar is $2 \text{ } \mu\text{m}$.

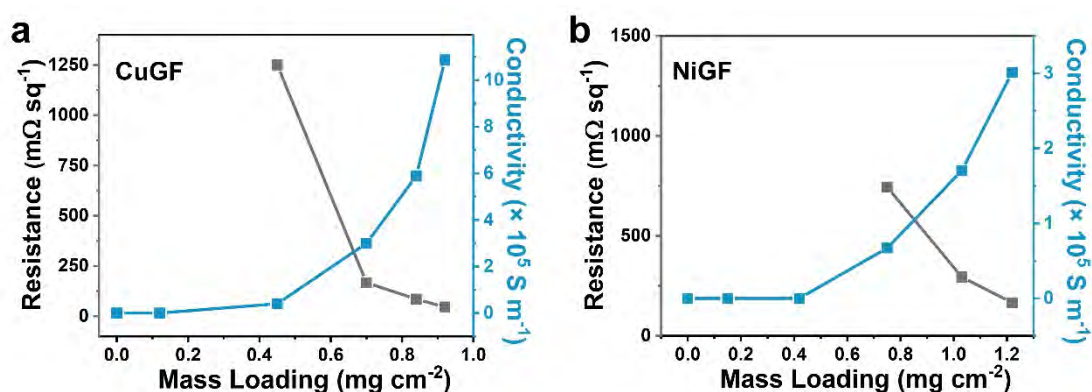


Figure 4.4 Correlation between the conductivity and mass loading of a) CuGF and b) NiGF.

Another important metric for current collectors is mechanical performance, especially for flexible applications. The basic requirement of current collectors for industrial fabrications of electrodes is 100 MPa because they must withstand the tension in roll-to-roll manufacturing. All the GF samples show tensile strengths higher than 150 MPa

and the results indicate that the PAMD method is a non-destructive method (Figure 5a). MGFs exhibit much better conductivity stability than metal foils (Figure 5b). In a bending radius of 2 mm, Cu foil and Al foil break at the 1670th and 434th cycle, respectively. On the contrary, MGFs maintain their high conductivity even after 10,000 bending cycles.

More and more attention is focused on the safety of the batteries. We also test the fire resistance of our MGFs. After ignition, both the CuGF and the NiGF do not catch fire (Figure 4.6). As the temperature reaches higher than the melting point of glass fiber fabric, the fiber structure is destroyed.

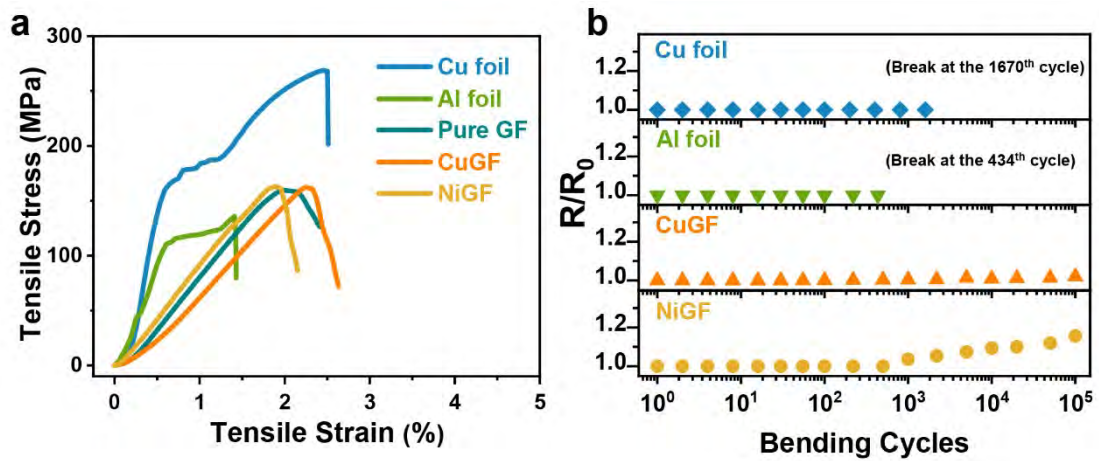


Figure 4.5 a). Typical stress-strain curves for Cu foil, Al foil, pure GF, CuGF and NiGF. b) Conductivity variations during the bending process for Cu foil, Al foil, CuGF and NiGF. The bending radius is 2 mm.

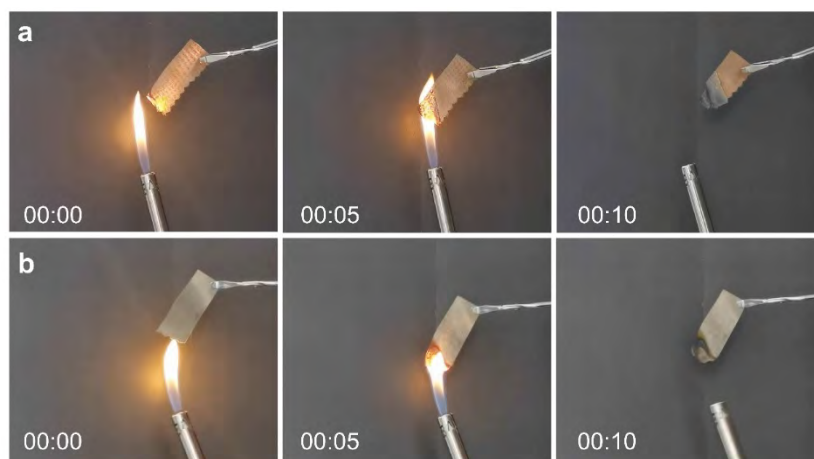


Figure 4.6 Fire-resistance test for a) CuGF and b) NiGF.

4.3.2 Electrochemical Performances of MGF-based Electrodes and LIBs

CuGF was then used as the current collector in the anode and the Gr was coated onto it by blade-coating method. As shown in Figure 4.7, the charge/discharge curves of the CuGF/Gr electrode exhibit similar features to the Cu/Gr electrode, indicating that CuGF is electrochemically stable without side reactions. It is noticed that CuGF/Gr electrode has a higher specific capacity than the Cu/Gr electrode at the first charge/discharge cycle, which is derived from a larger electrochemical surface area (ECSA) of CuGF. At different areal capacities of 1.2 mAh cm^{-2} , 1.8 mAh cm^{-2} , 2.4 mAh cm^{-2} and 3.0 mAh cm^{-2} , the specific capacities of these CuGF/Gr electrodes also show neglectable differences compared to the Cu/Gr electrodes (Figure 4.7b). When the weight of the whole electrode is considered, the electrode capacities of CuGF/Gr demonstrate significant enhancements of 94%, 57%, 43% and 40%, because of the significant cutting on the weight of current collectors. Moreover, CuGF/Gr electrode

exhibits comparable rate performance to the Cu/Gr electrode from 0.05 C to 1 C (Figure 4.7c). Cycling tests show that only 3.3% capacity decay after 200 charge-discharge cycles for the CuGF/Gr electrode (Figure 4.7d and 4.7e). The average capacity retention of the CuGF/Gr electrode reaches a high value of 99.97% for every cycle, illustrating that CuGF is as stable as Cu foils in long-term cycling.

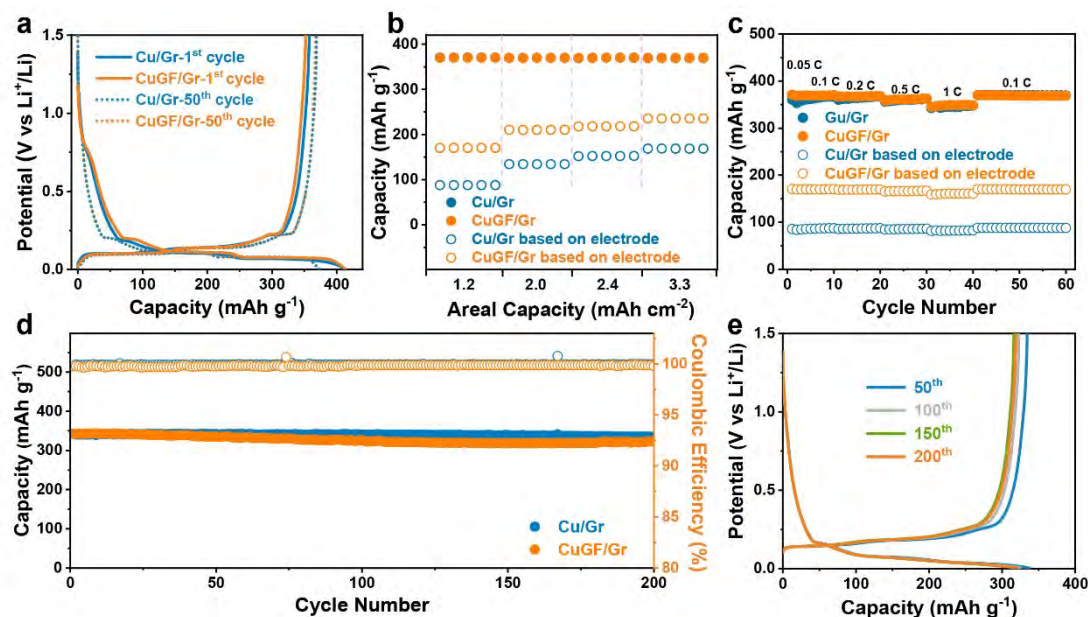


Figure 4.7 The galvanostatic charge–discharge (GCD) curves of the Cu/Gr and CuGF/Gr electrodes. b) Calculated capacities at different mass loading of Gr based on the active materials, or the whole electrode. c) Rate performance of the Cu/Gr and CuGF/Gr electrodes and specific capacities calculated based on the whole electrode. d) Cycle performance of the Cu/Gr and CuGF/Gr electrodes at 0.5 C and e) corresponding GCD voltage profiles of the CuGF/Gr electrode.

The light weight, high stability, and excellent electrochemical property of MGFs provide a significant superiority in fabricating energy-dense FLBs. Theoretically, a high

decrease of 10% in total weight can be achieved by only replacing the Cu foil with CuGF for a battery with the areal capacity of 2 mAh cm⁻² (the weight of anode, cathode, current collectors and separator are taken into account). As a proof of concept, three commonly used cathode materials, LFP, LCO and NCM were paired with the CuGF/Gr electrode. The energy densities are calculated based on the total weight of active material layer (including the binder and conductive agent), separator and electrolyte (2.0 mg mAh⁻¹). As shown in Figure 4.8b and Table 4.1, significant improvements of 16~18% of energy density have been realized in batteries using single-side-coating electrodes after replacing metal foils with MGFs. When using double-side-coating electrodes, it still manifests ~10% of increase. For example, the single-side-coated CuGF/Gr||NCM/Al full cell delivers an energy density of 198 Wh kg⁻¹, which is 18% higher than that of Gr/Cu||NCM/Al (168 Wh kg⁻¹), while the double-side-coated CuGF/Gr||NCM/Al full cell shows a high energy density of 221 Wh kg⁻¹. Similar results are obtained when paired with commercialized LFP and LCO electrodes (Table 4.1).

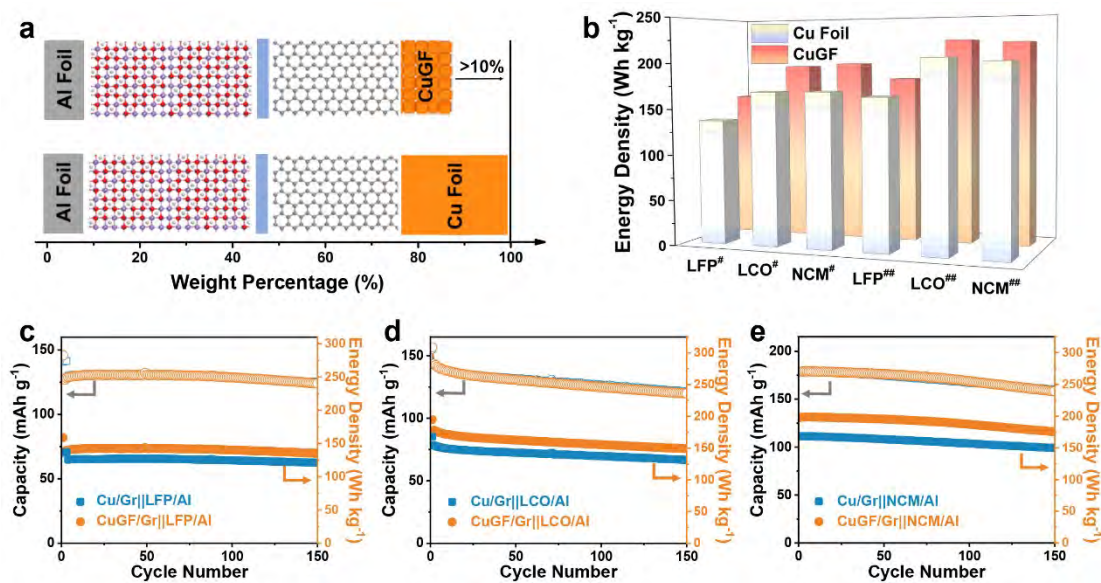


Figure 4.8 a) Schematic illustration of improvement by replacing the Cu foil with CuGF. b) Comparison of energy density between the cells using CuGF and Cu foil as current collectors. c-e) Cycle performances of full cells using CuGF/Gr and Cu/Gr anodes paired with Al/LFP, Al/LCO and Al/NCM cathodes.

Table 4.1 Summary of the properties of LIBs made with commercial metal foils and MGFs.

	Battery Type	Anode (mg cm ⁻²)	Cathode (mg cm ⁻²)	E _g [#] (Wh kg ⁻¹)	Improvement [#] (%)	E _g ^{##} (Wh kg ⁻¹)	Improvement ^{##} (%)
LFP	CuGF/Gr LFP/Al	9.0	17.1	159	17	180	10
	Cu/Gr LFP/Al	13.6	17.4	136	NA	164	NA
LCO	CuGF/Gr LCO/Al	9.4	14.6	195	16	223	9
	Cu/Gr LCO/Al	14.1	14.6	168	NA	205	NA
NCM	CuGF/Gr NCM/Al	11.2	18.1	198	18	221	10
	Cu/Gr NCM/Al	15.1	16.9	168	NA	201	NA

Importantly, using MGFs does not change the electrochemical mechanism and/or deteriorate the electrochemical performances of LIBs. The charging/discharging profiles and cyclic stabilities of LIBs using CuGF exhibit identical behavior with those using Cu foils. All LIBs retain more than 90% of their initial capacities after 150 charging/discharging cycles at 0.5C (Figure 4.8c-4.8e).

4.3.3 Flexibility Tests for Pouch Cells using MGFs.

Different from the flat metal foils, MGFs have a three-dimensional hierarchical structure which not only endows the MGFs with outstanding mechanical strength but also increases the interfacial adhesion between MGFs and the active material layer. Both CuGF/Gr and NiGF/LCO electrodes exhibit higher interfacial shear stress than Cu/Gr and Al/LCO electrodes (Figure 4.9b). It is important for flexible applications because the interface is always the weak spot for an electrode under deformations. Both CuGF and NiGF display slight decays of interfacial shear stress after 50 charging/discharging cycles, demonstrating durable interfacial adhesion between MGFs and active materials (Figure 4.9c and 4.9d).

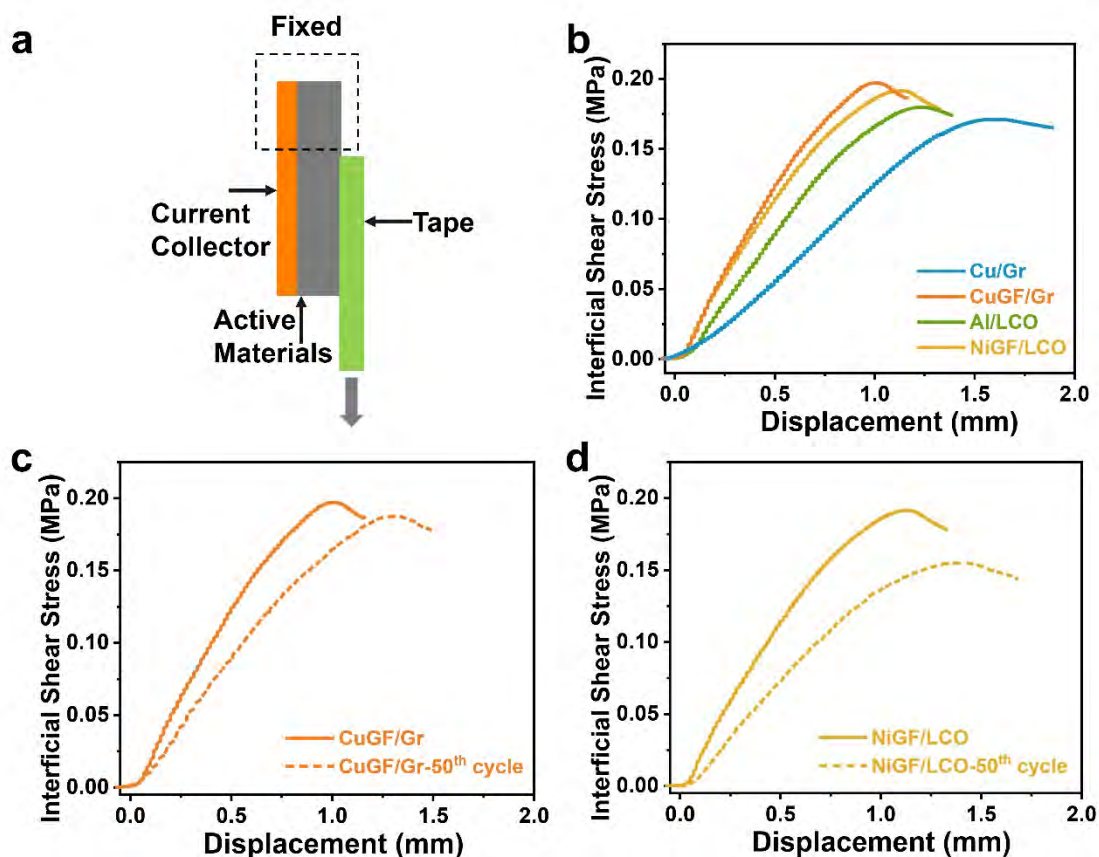


Figure 4.9 a) Setup for the single-lap shear tests. b) Results of interfacial shear stress tests for the Cu/Gr, CuGF/Gr, Al/LCO and NiGF/LCO electrodes. c, d) Comparison of interfacial shear stress of CuGF/Gr and NiGF/LCO electrodes before and after cycling.

MGF-based electrodes are bent at the bending radius of 2mm and in-situ observations are shown in Figure 4.10. From the cross-sectional SEM, we noticed that the active material layer tightly adheres to MGFs even under such a rigorous situation. Top view SEM images clearly show that no cracks or defects are found on the active material layer, demonstrating that MGF-based electrodes have outstanding flexibility.

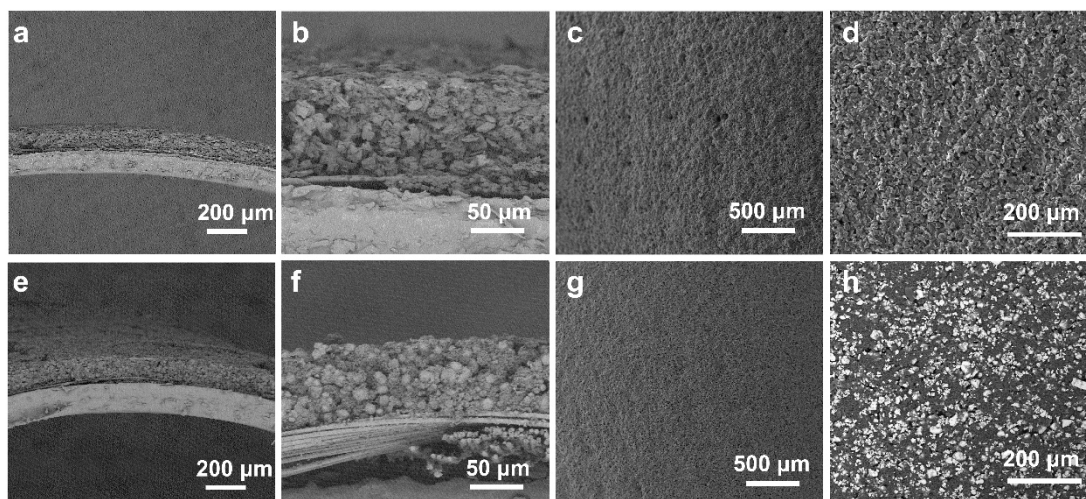


Figure 4.10 a, b) Cross-section and c, d) top-view SEM images of CuGF/Gr electrode of under bending radius of 2mm. e, f) Cross-section and g, h) top-view SEM images of NiGF/LCO electrode under bending radius of 2mm

The electrical conductivity variations during deformations are vital for flexible electrodes. After 10,000 bending cycles at a bending radius of 2 mm, the resistances of CuGF/Gr, and NiGF/LCO electrodes only increase by 3% and 8%, respectively (Figure 4.11a). Then the pouch cell using CuGF/Gr and NiGF/LCO electrodes was assembled, and its flexibility was tested. EIS results show that there is nearly no change in the internal resistance of the pouch cell at different states including under a rigorous bending radius of 2 mm (Figure 4.11b). In addition, only a slight decrease in electrochemical activity was observed in CV curves (Figure 4.11c).

As a result of high electrochemical stability and high flexibility, pouch cell using MGFs shows a high capacity retention of 94.1% after 1000 bending cycles at bending radii of 5 mm and 2 mm (Figure 4.11d). The GCD curves of the bent cell are similar to that in flat state, implying that no deterioration in the electrochemical process occurs and the capacity decay is from the loss of Li source (Figure 4.11e).

Here, we apply a parameter, the figure of merit of flexible battery (fb_{FOM}) to quantitatively compare the comprehensive performances among different flexible batteries. It is an indicator that reflects the areal energy density and flexibility of the battery. Our MGF-based FLBs display a high fb_{FOM} of 53.4, significantly higher than industrial products made with metal foils, and literature reported FLBs using soft structure or soft materials strategies (Figure 4.11f, Table 4.2). Such a high fb_{FOM} is attributed two aspects, the reasonable flexibility of MGF-based electrodes and ultralow areal density of MGFs.

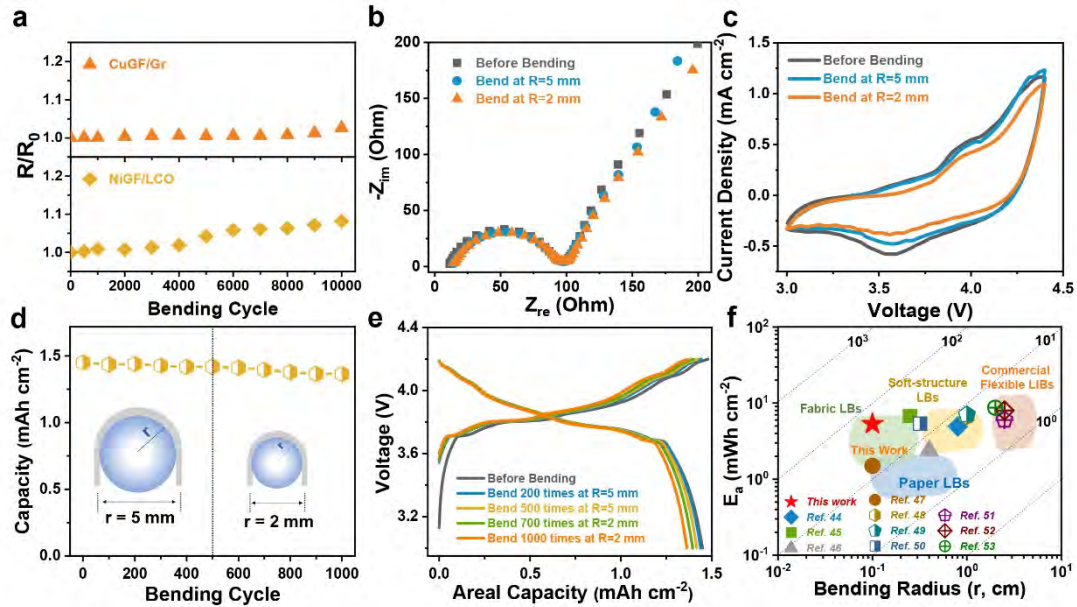


Figure 4.11 a) Conductivity variations during the bending process (bending radius is 2 mm) for CuGF/Gr and NiGF/LCO electrodes. b) The Nyquist plots and c) CV results of the CuGF/Gr||LCO/NiGF full cell at different bending radii. d) Cycle performance of the CuGF/Gr||LCO/NiGF full cell after bending cycles at radii of 5 mm and 2 mm and e) corresponding GCD curves. f). Comparison on fb_{FOM} of FLBs using similar electrode materials. The detailed calculations are listed in Table 4.2.

Table 4.2. Comparison of our flexible lithium battery with some best-performed flexible batteries reported in literatures.

Device	CC ^{a)}	Weight of CC	Weight of electrode	Capacity (mAh cm ⁻²)	E_g (Wh kg ⁻¹)	E_A (mWh cm ⁻²)	R (mm)	fb_{FOM}	Ref.
Gr/CuGF LCO/NiGF	CuGF,	2.9	9.8	1.5	185	5.34	1	53.4	This work
	NiGF	3.2	15.7						
Li/AuCF LCO/CF ^{b)}	Metallic	12.5	NA	1.45	NA	4.93	8	6.2	[198]
	CF	12.5							
Li/preLi-CC LFP/Al ^{c)}	preLi-CC	12.5	NA	2.05	167	6.8	2.5	27.2	[199]
	Al	4.2							
LTO/CNT LCO/CNT	CNT	0.13	13.5	~1.0	91.9	~2.4	4	6.3	[200]
		0.13	12.6						
LTO/GP LCO/GP ^{d)}	Grphene	1.8	6.8	NA	108	~1.5	1	15	[201]
		1.8	7.0						
Gr/Cu//LCO/Al	Metal Foil	7.5	NA	1.78	169	6.73	10	6.7	[50]
		4.2	16.5						
Gr/Cu LCO/Al	Metal Foil	9.0	NA	1.85	175	7.03	10	7.0	[117]
		4.2							
Gr/Cu NCM/Al	Metal Foil	7.5	7.5	1.45	167	5.37	3.2	16.8	[118]
		4.2	9.8						
Gr/Cu wire LCO/Al wire	Cu wire	NA	170 mg m ⁻¹	NA	86	NA	2	NA	[108]
	Al Wire	NA	94 mg m ⁻¹						
Flexible LIB (CG-062939)	Cu	NA	0.7 g	1.6	95	6	25	2.4	[202]
	Al	NA	(device)						
Flexible LIB (CG-063555)	Cu	NA	1.4	2.1	108	8	25	3.2	[203]
	Al	NA	(device)						
J-FLEX	NA	NA	NA	2.3	NA	8.7	20	4.4	[204]
Jenax Inc	NA	NA							

a) “CC” denotes “current collector” b) “CF” and “AuCF” denotes “carbon fabric” and “Au-coated carbon fabric”, c) “preLi-CC” denotes “pre-lithiated carbon cloth”, d) “GP” denotes “graphene paper”. The energy densities are calculated based on the total weight of the whole electrode.

4.4 Conclusions

In conclusion, MGFs are a type of lightweight, electrochemically stable, fire-resistant and flexible current collector. They surpass conventional metal foils in two crucial aspects, areal density and flexibility. MGFs only weigh ~40% of commercial metal foils, and possess excellent electrical conductivity and electrochemical stability. Therefore, the energy density can be improved by 9~18% for different cathode materials by replacing metal foils with MGFs, without deterioration on cyclic stability. MGFs are more flexible and mechanically durable than metal foils, resulting in stable conductivity during long-term bending test. As a result, the β_{FOM} of MGF-based flexible batteries reaches 53.4, around 20 folds higher than industrial products using metal foils. Furthermore, the preparation of MGFs is quite suitable for roll-to-roll fabrication in commercial LIBs' production line, which is meaningful to the large-scale production of FLBs.

Chapter 5. High-voltage Fabric-based Current Collectors for High-energy Flexible Batteries

In this Chapter, a high-voltage and flexible current collector is developed by a modified electroless deposition (ELD) method. Demand for energy-dense Li-ion batteries (LIBs) for flexible applications motivates us to fabricate a textile-based current collector with high anodic stability. Ni/P composite has been used as protecting material due to its anti-corrosion property and has been proven highly stable in battery systems. Hence, Ni/P is adopted as the coating layer on the glass-fiber fabrics (GFs) to endow the conductive fabrics with better electrochemical stability. The anodic current for Ni/P-coated GFs (NiPGFs) starts at ~ 4.7 V which is high enough for most cathode materials such as lithium cobalt oxide (LCO) and lithium nickel cobalt manganese (NCM). NiPGF/NCM electrodes exhibit lower areal density and better flexibility than Al/NCM electrodes while showing comparable rate and cycle performance. By eliminating the negative reactions by the atomic layer deposition (ALD) method, the full cell presents reasonable cyclic stability with 82.6% capacity retention after 200 charge/discharge cycles. Under an extreme and continuous bending at the radius of 5 mm, the output power is stable without apparent fluctuations for the pouch cell using NiPGF.

5.1 Introduction

LIBs have conquered the market due to their high energy density, low self-discharging, and other advantages.^{10, 28, 205} However, conventional current collectors for LIBs, Cu and Al foils are not mechanically robust to withstand continuous deformations in

flexible applications.^{206, 207} In this regard, researchers turned to using other soft materials or designing special structures to improve the flexibility of current collectors.¹⁷ Among these, textile-based current collectors are a promising candidate for flexible batteries. Compared to coating with carbon-based materials, metal-coated textiles are more competitive in view of conductivity.^{22, 23, 143, 145, 146} Considering the electrochemical stability, conductivity, density, and cost, Cu and Al are the best choices of current collectors for the anode and cathode, respectively. Nevertheless, the deposition of Al is rather complicated and is not feasible to scale up for industrial production.²⁰⁸⁻²¹¹ Hence, the Ni coating layer becomes the best substitute on the cathode side. Our group has reported some works using Ni-coated textiles as the current collectors for the cathode to fabricate flexible batteries, which exhibited high flexibility while maintaining stable operation.^{56, 139, 199}

On the other hand, high-voltage cathode materials are an important development direction to improve the energy density of LIBs further because the energy is proportional to the capacity and discharge voltage of the battery. Unfortunately, Ni is not electrochemically stable when the potential increase to 4 V (vs. Li/Li⁺), which means that Ni-coated current collectors are suitable for those active materials with cut-off voltage below 4 V (vs. Li/Li⁺), such as lithium iron phosphate (LFP). Therefore, it is urgently demanded to improve the anodic stability of flexible current collectors for those cathodes with higher cut-off voltage (NCM and LCO).

Ni/P composite has been widely used as protecting layer because of its unique anti-corrosion property. Its electrochemical stability was also evaluated by different works.²¹²⁻²¹⁴ Alternatively, we apply a modified electroless deposition (ELD) process to

introduce the P element into the Ni coating. The Ni/P-coated glass fiber fabrics (NiPGFs) display much higher anodic stability than Ni-coated ones. Further atomic layer deposition (ALD) method further prevents the negative reactions in the full cell using NiPGF, resulting in a stable operation of the NCM/Gr battery.

5.2 Experimental Part

5.2.1 Preparation of Ni/P Composite-coated Glass Fiber Fabrics (NiPGF)

The pre-treatments of GFs are totally the same as the process used for depositing Cu and Ni. After hydrophilization and silanization, [2-methacryloyloxy)ethyl]trimethylammonium chloride solution (METAC) was polymerized onto the surface of GFs. The $[\text{PdCl}_4]^{2-}$ catalyst was then anchored onto the GFs by an ion-exchange reaction. Detailed information can be referred to **Chapter 3** or **Chapter 4.2.1**.

The Ni/P composite plating was conducted in an ELD solution of $\text{Ni}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (40 g L^{-1}), sodium citrate (24 g L^{-1}), sodium acetate (24 g L^{-1}) in DI water. The pH was first regulated to ~ 4 through lactic acid. and then the sodium hypophosphite solution (24g L^{-1}) was added into the solution. The ELD process was conducted at 85 °C for 60-90 min, depending on the target conductivity and areal density.

5.2.2 Protection of NiPGF by atomic layer deposition (ALD) method

ALD method was utilized to protect the current collectors or electrodes by depositing

several-nanometer-thick Al_2O_3 . ALD was conducted at 80 °C in a thermal ALD system (Savannah, Veeco) and the deposition thickness of every cycle in this condition is 0.75 Å. Samples with different deposition cycles were prepared, and the resultant samples are named ALD-xx (xx indicates the deposition cycles). For example, ALD-20 is the sample of NiPGF treated with 20 ALD cycles.

5.2.3 Cell Assembly

The preparation details of electrodes and cell assembly can be found in **Chapter 3.2.3 and 3.2.4**, respectively.

5.2.4 Characterization

Morphology observations were conducted in a Scanning Electron Microscope (SEM, Tescan VEGA3). Elemental analysis was scanned by the Oxford energy dispersive x-ray (EDX) spectroscopy system. Battery performances were obtained by a battery test system (BTS 3000, Neware, China). Linear scanning voltammetry (LSV) and cyclic voltammetry (CV) were carried out by using an electrochemical workstation (Biologic, France). XPS analysis was carried out using an XPS system (Thermo Fisher Nexsa, USA). Detailed information can be referred to **Chapter 3**.

5.3 Results and Discussion

5.3.1 Fabrication and Anodic Stability of NiPGF

NiPGFs were fabricated by depositing Ni/P composite onto GFs by the polymer-

assisted metal deposition (PAMD) method. P element was introduced by the reductant of sodium hypophosphite to enhance the electrochemical stability of the cathode current collector. A dense Ni/P composite layer is coated onto every single fiber of the GFs and the thickness is around 500 nm (Figure 5.1a and 5.1b). EDX mapping results show that the distribution of Ni and P is very uniform on the surface of fibers (Figure 5.1c-f). The P content identified by EDX is ~15% (atomically). As the conductivity of Ni/P composite is a little bit lower than Ni, a deposition loading of 2 mg cm^{-2} was set here so the resultant NiPGF weighs 4 mg cm^{-2} .

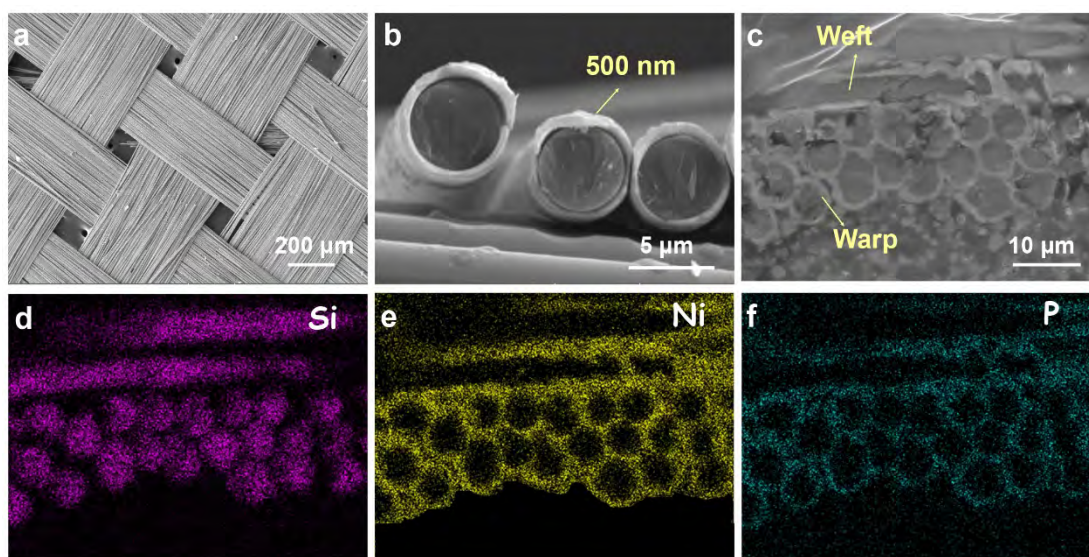


Figure 5.1 SEM images of a) the top view and b) cross-sectional view of NiPGF. c) SEM images of NiPGF immobilized in resin and d-f) corresponding EDX mapping of Si, Ni and P.

The anodic stability is very important for a current collector used in the cathode because operating a cell at a higher cut-off voltage delivers a higher energy density. As shown in Figure 5.2a, the anodic current density of NiGF sharply increases at the potential of 4 V vs. Li/Li^+ . In contrast, the oxidation current appears at $\sim 4.7 \text{ V}$ for the NiPGF, indicating a much higher anodic stability than Ni. Then, long-term stability in cyclic

test of NiPGF was carried out and the results show NiPGF are very stable in the range of 3-4.5 V vs. Li/Li^+ (Figure 5.2b). A schematic diagram of the potential and specific capacities is presented in Figure 5.2c. NiGF can only support LFP, a safe but low-energy cathode material. On the contrary, NiPGF can meet almost all the commercially used high-voltage cathode materials including the NCM, LCO and lithium nickel cobalt aluminum oxides (NCA).

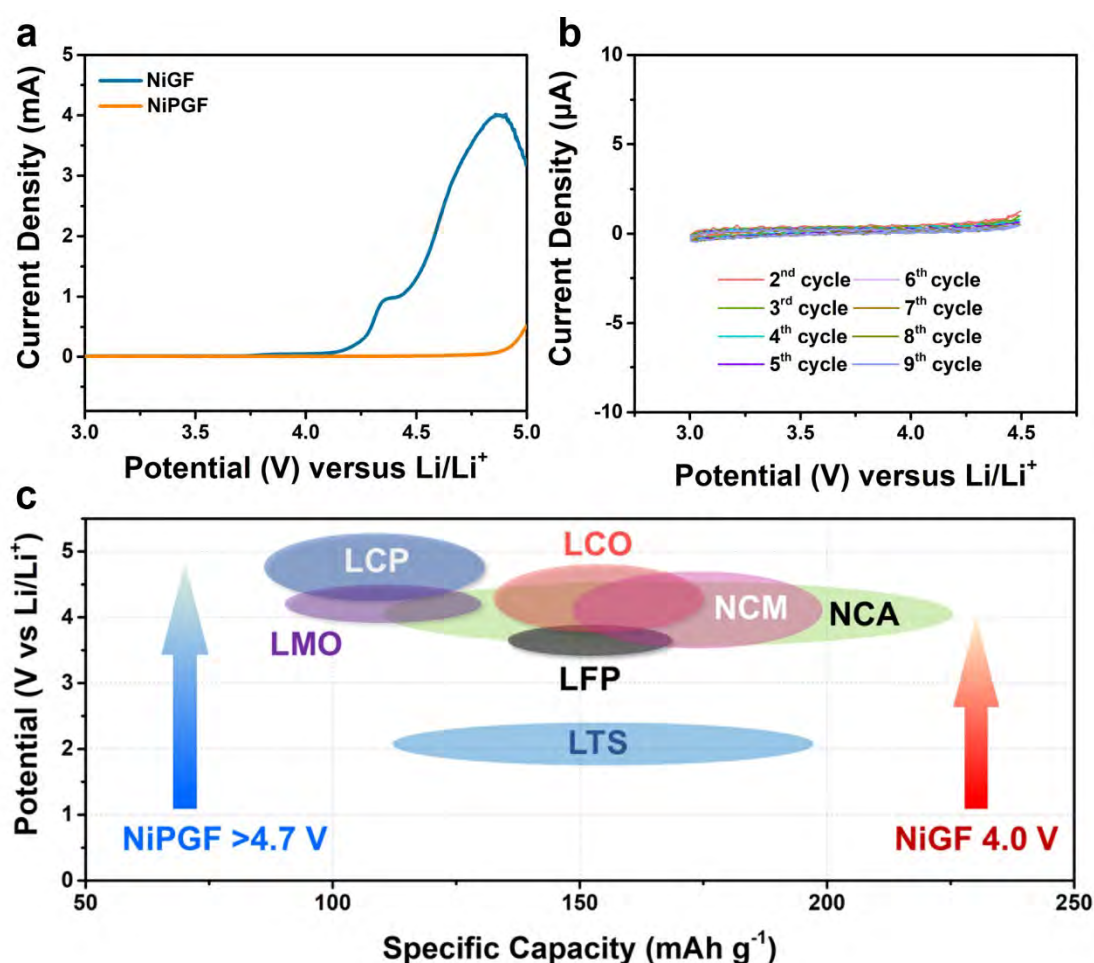


Figure 5.2 a) LSV curves of NiGF and NiPGF at a scan rate of 0.5 mV s^{-1} in the range of 3 to 5 V vs. Li/Li^+ . b) CV curves of NiPGF at a scan rate of 0.5 mV s^{-1} in the range of 3 to 4.5 V vs. Li/Li^+ . c) Schematic diagram of the working potential and specific capacity of commercially used cathode materials. LCP denotes lithium cobalt phosphate, LMO denotes lithium manganese, LTS denotes lithium titanium sulfide.

5.3.2 Electrochemical Performances of NiPGF-based Electrodes

Then, NiPGF was used as the current collector in the cathode. LFP and NCM were chosen as representative active materials to test the electrochemical performances of NiPGF-based electrodes. Outstanding properties are realized for the NiPGF/LFP electrode which has comparable rate and cycle performances to commercial Al/LFP electrode. NiPGF/LFP electrode retains about 90% capacity at a 1 C rate (144 mAh g⁻¹) when normalized versus a 0.1 C rate (160 mAh g⁻¹). The electrode also has a high capacity retention of 93.9% after 300 cycles at 0.5 C. As a result, the full cell of CuGF/Gr||LFP/NiPGF shows outstanding cyclic stability with capacity retention of 85.8% after 500 charge/discharge cycles. It means that the average capacity retention of every single cycle is 99.97%, demonstrating that NiPGF is an excellent flexible current collector for LFP.

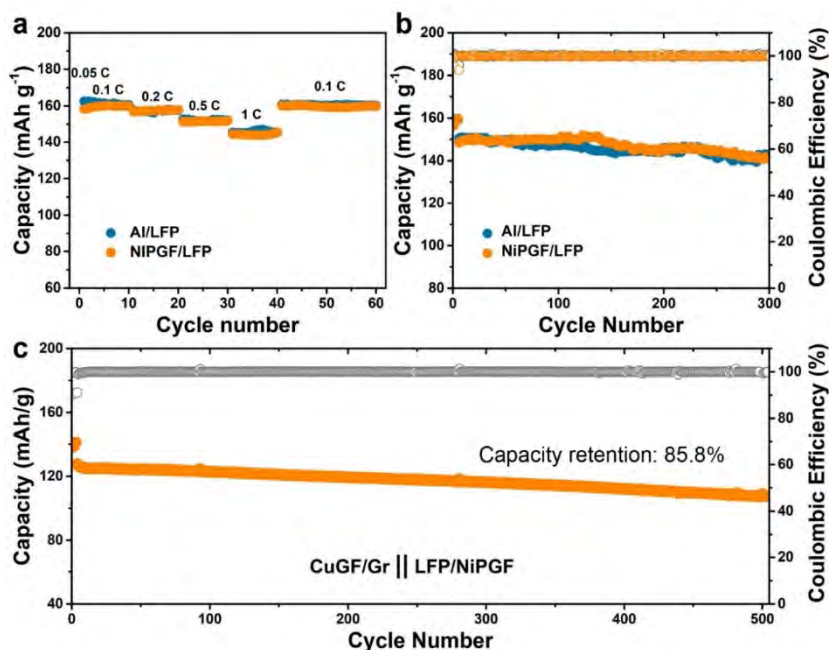


Figure 5.3 a) Rate and b) cycle performances of Al/LFP and NiPGF/LFP electrodes. c) Cycle performance of the full cell of CuGF/Gr||LFP/NiPGF.

NCM electrodes, as a high-voltage cathode material, are charged to 4.4 V (vs. Li/Li⁺) here, which is 0.4 V higher than the cut-off voltage of LFP. The half-cell tests of NiPGF/NCM electrodes are also satisfied. Similar rate capability and cyclic stability are realized for the NiPGF/NCM electrodes compared to the Al/NCM electrodes. During the long-term cycle tests, the CEs of NiPGF/NCM are also comparable to those of Al/NCM, which means there are no serious side reactions for NiPGF, even at a high potential. Beyond our expectations, when we paired NiPGF/NCM electrode with CuGF/graphite (Gr) electrode, a sudden failure happened at the ~70th cycle with disturbed CEs (Figure 5.4c). On the contrary, the full cell of CuGF/Gr||NCM/Al shows stable cycle performance, meaning that the NiPGF has some effects on the operation of the full cell but not the half cell. Also, it should be noticed that it happens at a high potential because the full cell of CuGF/Gr||LFP/NiPGF runs stably as mentioned before. Combined with the results of half-cell tests, an initial conclusion is that some matter dissolves from the NiPGF at high potential (4.4 V vs. Li/Li⁺), transfers to the anode side, and influences the electrochemical stability of the graphite electrode.

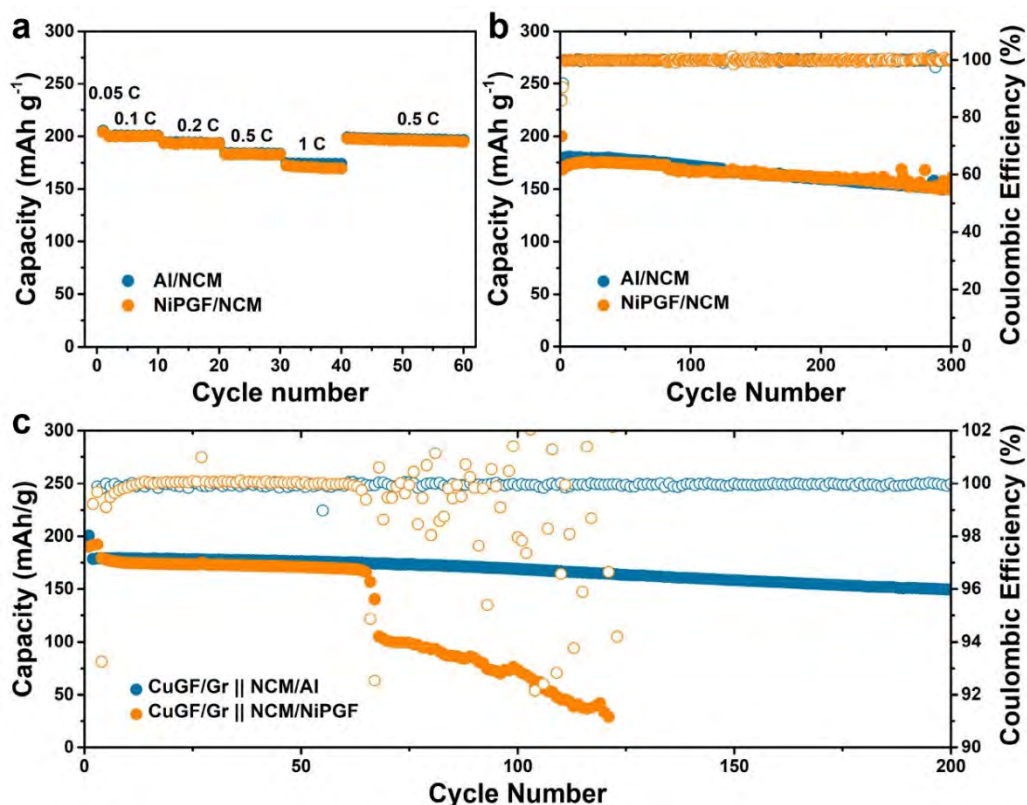


Figure 5.4 a) Rate and b) cycle performances of Al/NCM and NiPGF/NCM electrodes. c) Cycle performance of the full cell of CuGF/Gr||NCM/Al and CuGF/Gr||NCM/NiPGF.

5.3.3 Protection of NiPGF-based Electrode

To reveal the underlying mechanism of NiPGF-based full cell failure and protect the NiPGF-based electrode, a several-nanometer-thick layer of Al₂O₃ was deposited onto the NiPGF by the ALD method. Al₂O₃ will react with Li⁺ in the electrolyte to form a compound of Li_xAl_yO_z which acts as a physical screen except for Li⁺ (it is highly conductive for Li⁺). Because of the ultrathin thickness of this layer, the conductivity of NiPGF is not changed after the ALD process. It can further improve the anodic stability of the current collector (Figure 5.5a). With increased thickness, no oxidation current is triggered even at a high voltage of 5 V (vs Li/Li⁺) for ALD-60. In the continuous cycle tests between 3 to 4.5 V (vs. Li/Li⁺), the ALD sample shows stable electrochemical stability (Figure 5.5b).

After the protection of Al_2O_3 layer, the cyclic performance of the full cell of $\text{CuGF/Gr}||\text{NCM/NiPGF}$ improved a lot. No sudden failure is observed for all the full cells using ALD samples. ALD-40 shows the best cyclic stability and a high capacity retention of 82.6% after 200 cycles (Figure 5.5c). The results prove again that something harmful to the battery operation will be dissolved from NiPGF and the Al_2O_3 can effectively prevent this phenomenon.

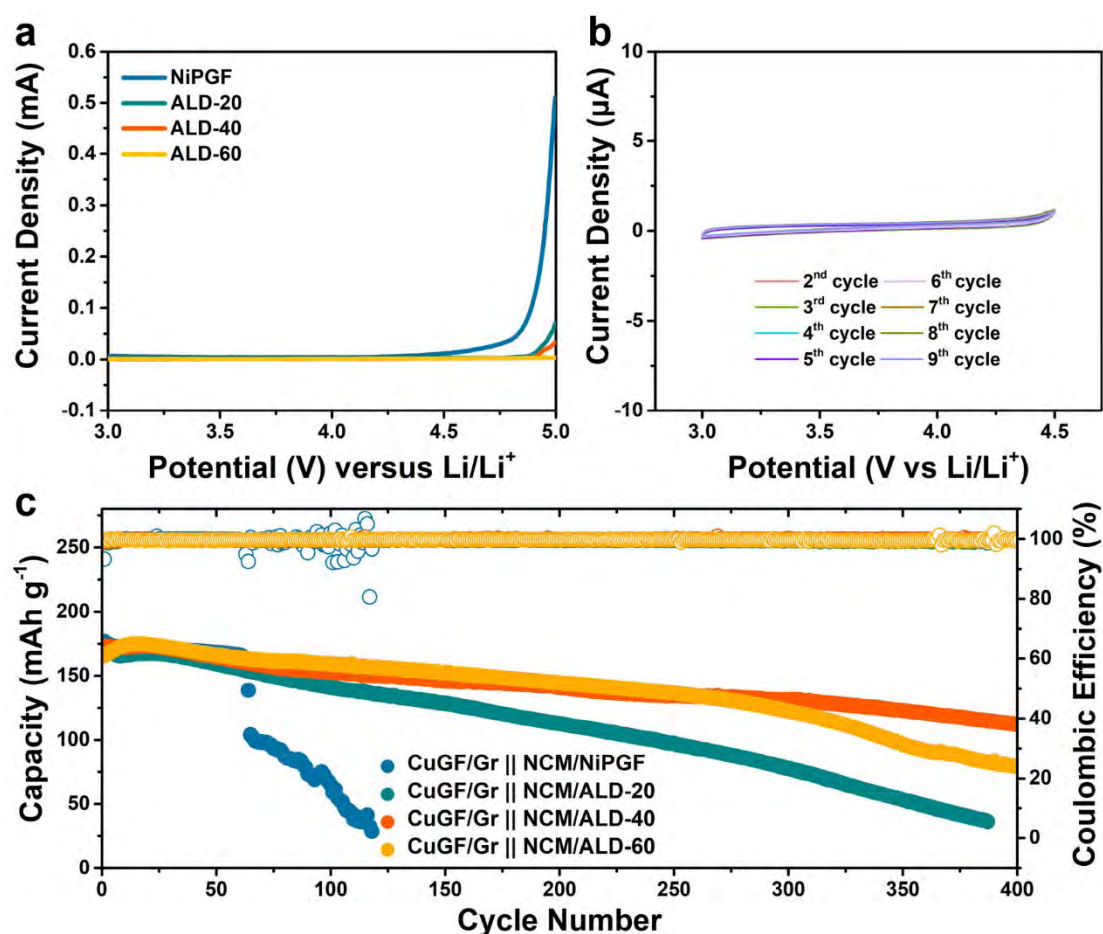


Figure 5.5 a) LSV curves of NiPGF and ALD samples at a scan rate of 0.5 mV s^{-1} in the range of 3 to 5 V vs Li/Li^+ . b) CV curves of ALD-40 at a scan rate of 0.5 mV s^{-1} in the range of 3 to 4.5 V vs Li/Li^+ . c) Cycle performances of the full cells of $\text{CuGF/Gr}||\text{NCM/NiPGF}$ and $\text{CuGF/Gr}||\text{NCM/ALD}$ samples.

XPS characterization was carried out to obtain the component information of the solid electrolyte interface (SEI) layer at the graphite anode. The peak corresponding to the Li_2CO_3 appears for all the full cells using ALD samples except for the cell using the original NiPGF current collector (Figure 5.6a-d). In the F 1s spectra, the components change regularly with the increased thickness of the Al_2O_3 layer (Figure 5.6e-h). The content of LiF continuously increases while the content of Li_xPF_y decreases to even zero for the ALD-60 sample. Such an inorganic-rich SEI layer with higher content of Li_2CO_3 and LiF is much more stable so the cyclic stability of batteries using ALD samples improved a lot compared to the battery using NiPGF.

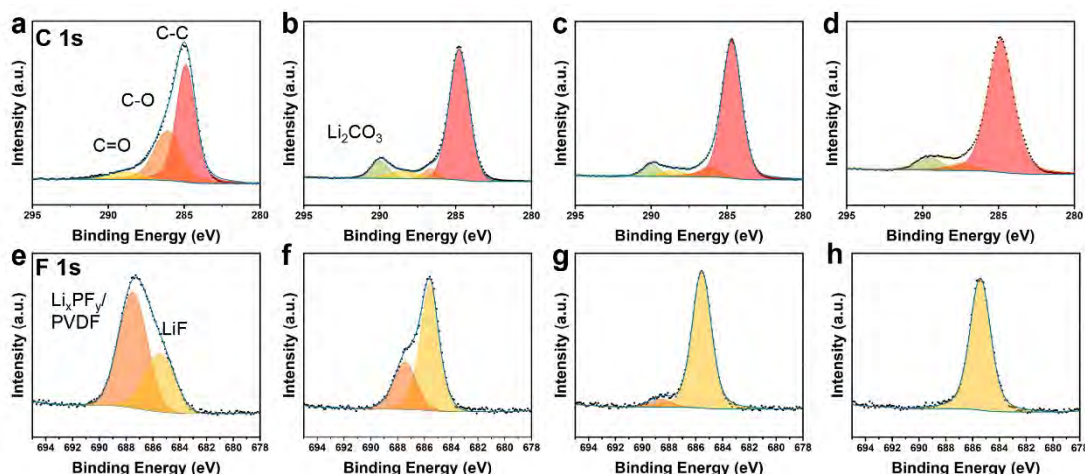


Figure 5.6 C 1s high-resolution XPS spectra of the anode surface in the cycled full cell with the cathode current collector of a) NiPGF, b) ALD-20, c) ALD-40 and d) ALD-60. F 1s high-resolution XPS spectra of the anode surface in the cycled full cell with the cathode current collector of e) NiPGF, f) ALD-20, g) ALD-40 and h) ALD-60.

5.3.4 Mechanism of the failure of the NiPGF-based full cell

The variation of the SEI layer reminds us of a widely reported failure model of NCM material that the SEI layer contaminated by the transition metals (TMs) leads to fast capacity fading and collapse of the full cell. It starts from the dissolution of TMs, which then transfer to the anode side, and deposit onto the surface of graphite. Hence, full cells using NiPGF current collectors were disassembled after battery cycles to check the surface components of the graphite anode (Figure 5.7a and 5.7b). To distinguish the Ni from NCM and the Ni from NiPGF, LCO was used as cathode material as well. We found that there is no Ni element on the anode (or the content of Ni is too low to be detected by EDX) for the CuGF/Gr||LCO/NiPGF but a little Ni is detected for the CuGF/Gr||NCM/NiPGF. It means that the dissolution of Ni from NiPGF is very little, at least less than the dissolution amount from the NCM material. Moreover, we noticed that the CuGF/Gr||LCO/NiPGF full cell also shows a sharp capacity decline after ~70th cycle with decreased CEs. Combining the results of EDX mapping and the cell performances, we can conclude that cross-talk of Ni is not the major cause of this failure, or at least not just the Ni ions cause the rapid capacity fade.

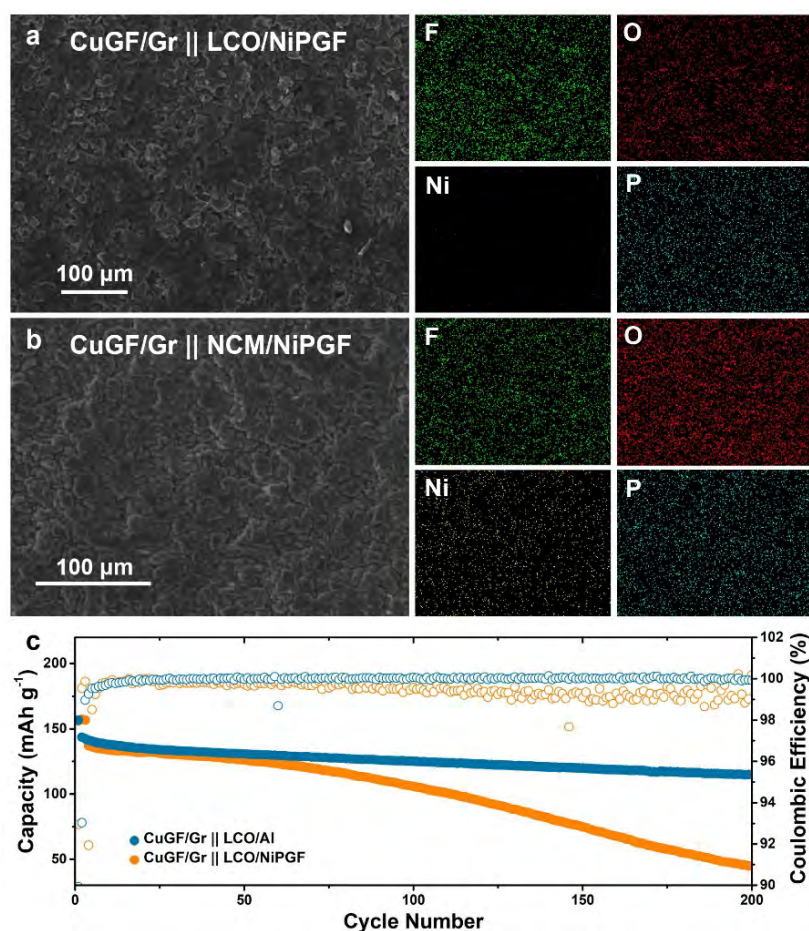


Figure 5.7 a) SEM image of the anode surface in a cycled full cell of CuGF/Gr||LCO/NiPGF and corresponding EDX mapping images. b) SEM image of the anode surface in a cycled full cell of CuGF/Gr||NCM/NiPGF and corresponding EDX mapping images. c) Cycle performances of full cells of CuGF/Gr||LCO/Al and CuGF/Gr||LCO/NiPGF.

To figure out the failure mechanism of NiPGF-based full cell, the original NiPGF, cycled NiPGF and ALD protected NiPGF were analyzed by the XPS. In the freshly prepared NiPGF, Ni element exists as simple substance and Ni²⁺ states while P exists as simple substance and phosphorus oxide states (Figure 5.8a and 5.8d). After battery cycles, the relative content of Ni²⁺ and P simple substance decreases without generating other matter (Figure 5.8b and 5.8e). It implies that both Ni²⁺ and P are dissolved in the

electrolyte during battery cycles. As the detection limit of XPS is only several nanometers, signals of Ni and P are weakened a lot, indicating that the Ni/P composite is covered by Al_2O_3 successfully (Figure 5.8c and 5.8f).

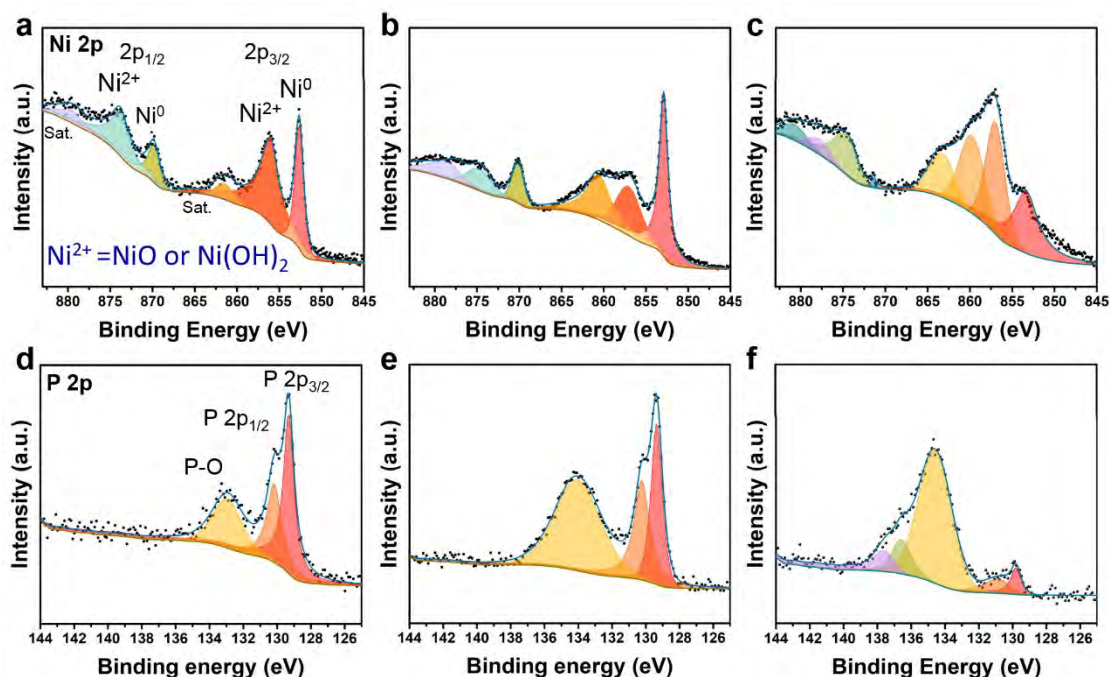


Figure 5.8 Ni 2p high-resolution XPS spectra of a) as-prepared NiPGF, b) cycled NiPGF and c) as-prepared ALD-40. P 2p high-resolution XPS spectra of d) as-prepared NiPGF, e) cycled NiPGF and f) as-prepared ALD-40.

The element characterization of the separators can indirectly reflect the contents of Ni and P dissolved in the electrolyte. In the cell using NiPGF, high intensities of Ni and P are detected because the NiPGF is exposed to the electrolyte (Figure 5.9a-c). After the coating of the Al_2O_3 , the signal of Ni disappears and the intensity of the P peak also declines sharply (Figure 5.9d-f), demonstrating that the Al_2O_3 can prevent the dissolution of Ni and P by acting as a “physical wall” between the NiPGF and the electrolyte.

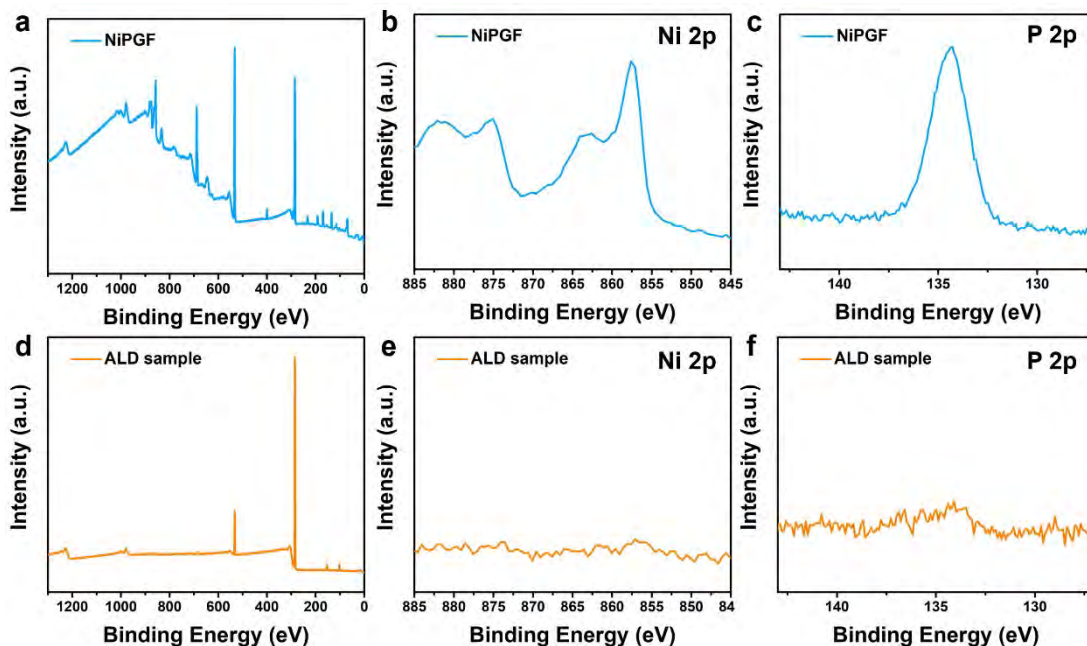


Figure 5.9 a) Full XPS spectra, b) Ni 2p and c) P 2p spectra of separator in the cycled full cell using NiPGF as cathode current collector. d) Full XPS spectra, e) Ni 2p and f) P 2p spectra of separator in the cycled full cell using ALD-40 as cathode current collector.

At last, Ni and P appear in the anode side for all the cells no matter NiPGF or ALD samples are used (Figure 5.10). It should be noticed that the intensities of Ni peak are comparable for different samples. The quantitative results also show that the Ni content is 2-3 at% and ALD sample-based cells have a little lower Ni content than NiPGF-based cell (Table 5.1). However, a high content of 6.77 at% of P is observed in the anode side for the cell using NiPGF. This value sharply decreases to ~1 at% for the cells using ALD samples. Considering that the LiPF₆-derived SEI also contains the P, we think that the extra P is originated from the NiPGF and dissolution can be blocked by Al₂O₃.

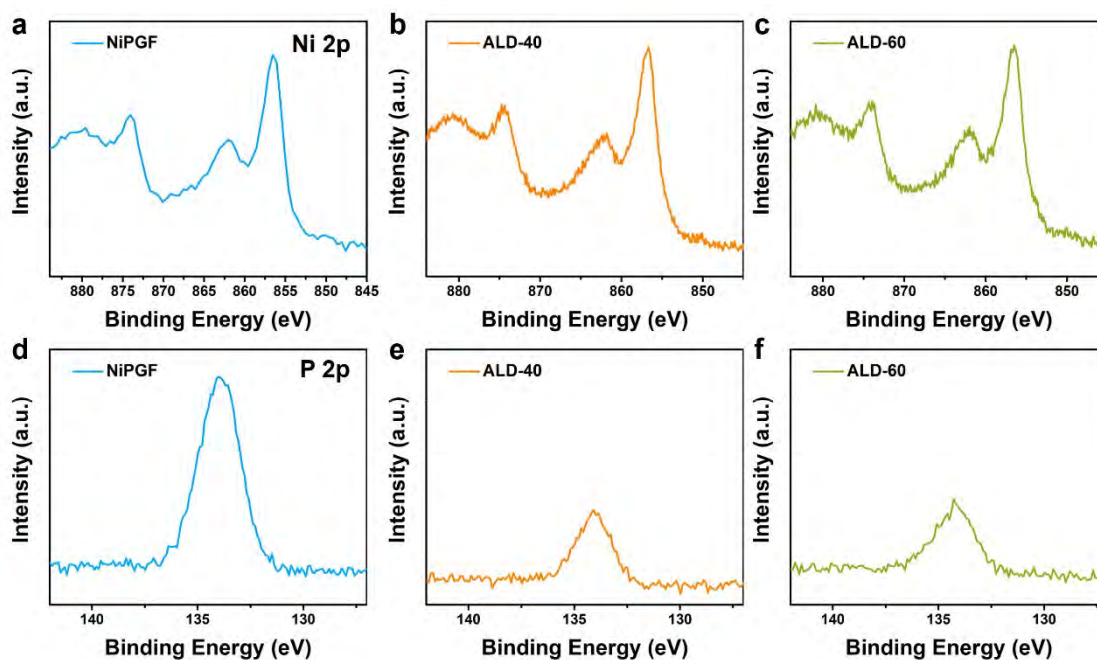


Figure 5.10 Ni 2p high-resolution XPS spectra of the anode surface in the cycled full cell with the cathode current collector of a) NiPGF, b) ALD-40 and c) ALD-60. P 2p high-resolution XPS spectra of the anode surface in the cycled full cell with the cathode current collector of d) NiPGF, e) ALD-40 and f) ALD-60.

Table 5.1 Atomical content of Ni and P at the anode side.

	Ni	P
NiPGF	2.93 at%	6.77 at%
ALD-40	2 at%	0.84 at%
ALD-60	2.44 at%	1.08 at%

As a common cognition, phosphorous is a kind of anode material with the lithiation and de-lithiation occur during the range of 0.005-2 V (vs. Li/Li⁺). Hence, CV and GCD tests were conducted for the prepared NiPGF current collector to see the electrochemical response of phosphorous in NiPGF (Figure 5.11). There are four distinct cathodic peaks and three anodic peaks in the first cycle. The peak located at ~1.3 V is attributed to the

reduction of electrolyte and SEI formation process. The remaining peaks centered at ~ 0.75 V, 0.6 V and 0.4 V indicate the different states of Li_xP . The shifts of the lithiation and de-lithiation peaks of P may be ascribed to the change of chemical environment. Al_2O_3 -coated NiPGF shows a capacitance-like behavior that the cathodic and anodic peaks are very weak (Figure 5.11b). It demonstrates again that the NiPGF is successfully protected by the ALD method. In the first cycle of GCD curves, NiPGF exhibits three plateaus, which reasonably correspond to the CV results (Figure 5.11c). The low capacity is derived from the low content of the available P for the ALD sample, which presents lower capacities than NiPGF in long-term cycling (Figure 5.11d). The results illustrate that the reversible electrochemical reaction of the P occurs continuously.

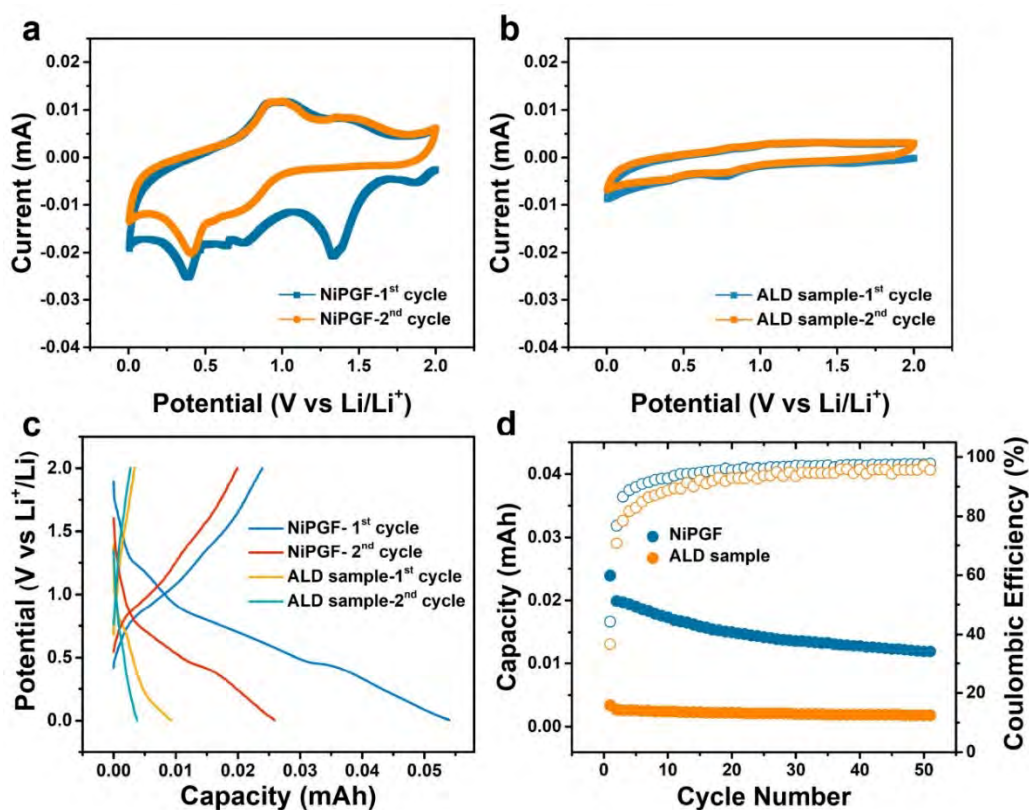


Figure 5.11 CV curves of a) NiPGF and b) ALD-40 at a scan rate of 0.1 mV s⁻¹ in the range of 0.005 to 2 V (vs. Li/Li^+). c) Galvanostatic charge-discharge (GCD) curves and d) cycle performance of NiPGF and ALD-40.

The failure and protection mechanism of NiPGF-based electrodes and full cells are schematically illustrated in Figure 5.12. It starts from the dissolution of the P at a high potential and then it transfers from the cathode side to the anode side. The continuous cycling of these foreign P on the anode side affects the SEI layer of the graphite anode. As known for us, the lithiation and de-lithiation of P are accompanied by a significant volume change which causes the break of the SEI layer. In every cycle, the electrolyte will decompose and react to form the SEI again with fast and irreversible Li loss. By covering with Al_2O_3 , shuttling of P is significantly prevented, leading to a more stable SEI layer of graphite anode. As a result, all the ALD samples have an inorganic-rich SEI layer and much better cyclic performance than the NiPGF-based full cell.

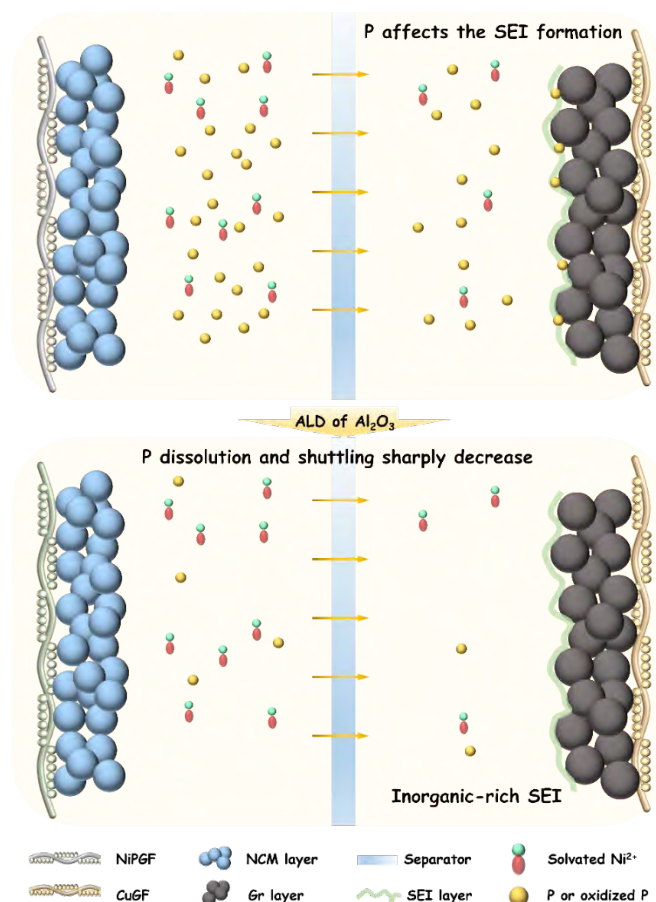


Figure 5.12 Schematic illustration of the failure and protection mechanisms of NiPGF-based full cells.

5.3.5 Flexibility tests for the electrodes and pouch cell

The flexibility of the metal-coated GFs (MGFs) and MGF-based electrodes are evaluated by bending test at a bending radius of 4 mm. The conductivity changes of ALD-protected NiPGF and CuGF after 10,000 bending cycles are lower than 20% (Figure 5.13a and 5.13b). Metal coating layers on the GFs keep intact without obvious cracks. Such excellent mechanical robustness may be attributed to the intermediate layer of the polymer.

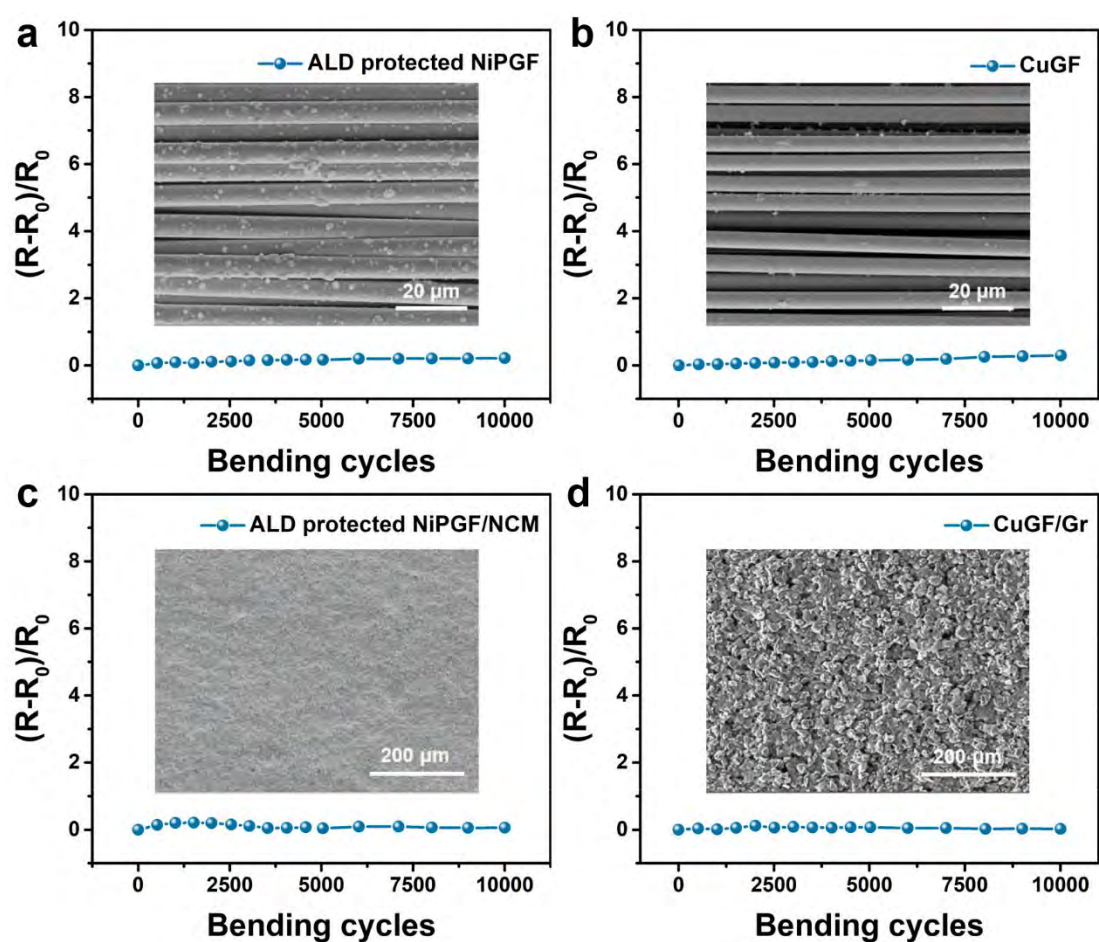


Figure 5.13 Electrical conductivity variation as a function of bending cycles for a) ALD-protected NiPGF, b) CuGF, c) ALD-protected NiPGF/NCM and d) CuGF/Gr. Insets are SEM images of surface morphology after bending tests. The bending radius of curvature is set to 4 mm.

The conductivity stability of the current collector is the prerequisite of a highly flexible electrode. The hierarchical structure of fabrics endows a better interfacial binding between the active material composite layer and the current collectors. As a result, both the NCM and Gr composite electrode layers remain integrated, resulting in stable conductivities of ALD-protected NiPGF/NCM and CuGF/Gr during the 10,000 bending cycles (Figure 5.13c and 5.13d).

Motivated by the excellent mechanical durability of MGF-based electrodes, ALD-protected NiPGF/NCM was paired with CuGF/Gr to assemble the pouch cell (Figure 5.14a-e). To better simulate the practical use of a flexible battery, a dynamic bending test was conducted that the charge/discharge processes are operated during bending cycles. At a bending radius of 5 mm, our pouch cell using ALD-protected NiPGF and CuGF runs stably without apparent potential fluctuations (Figure 5.14f). Compared to the flat state, a little lower capacity was discharged, about 92.8% of the capacity in the flat state. The result indicates that the MGF-based pouch cell can not only provide a stable voltage output but also maintain a high percentage of original capacity, under harsh deformation.

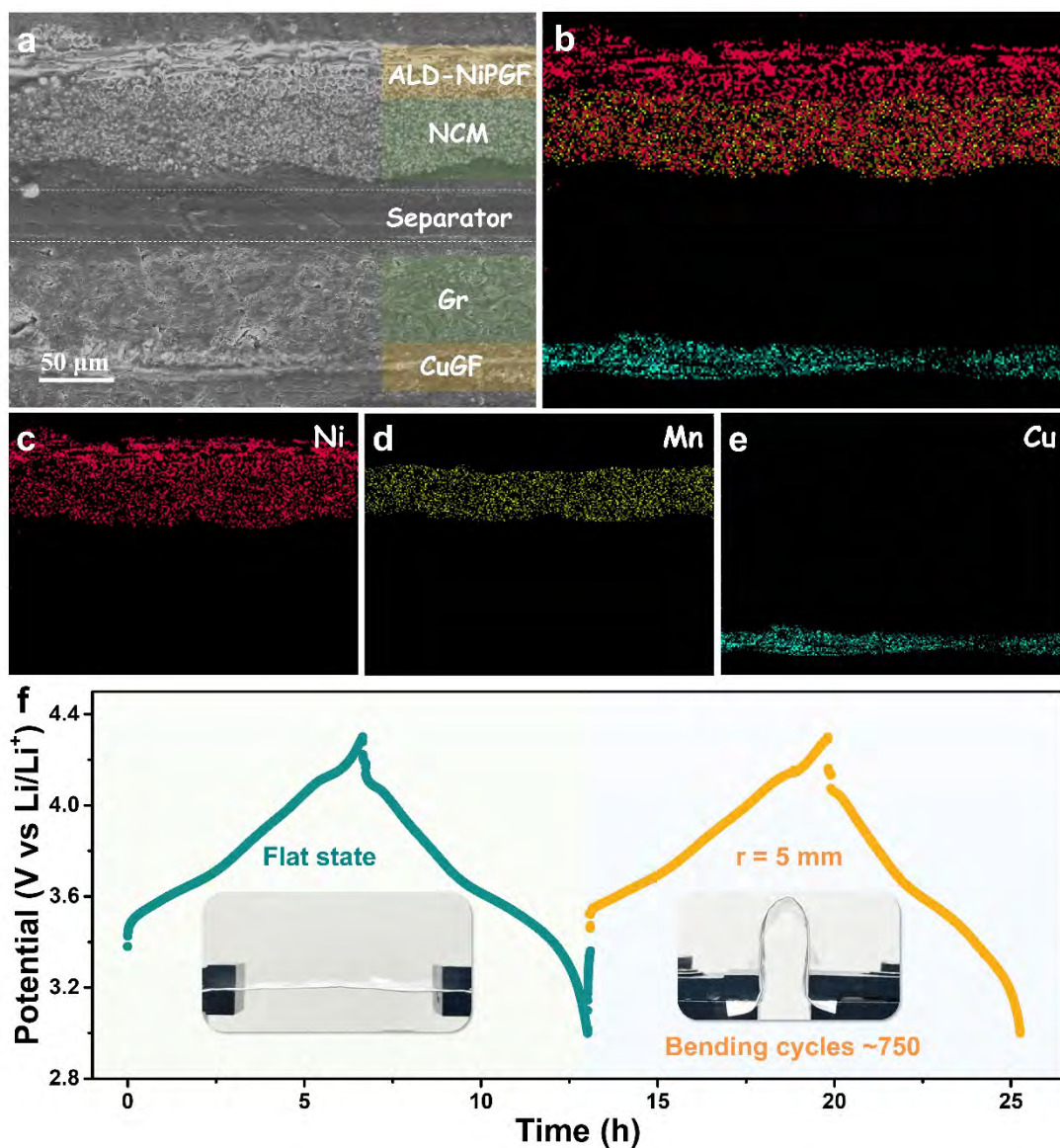


Figure 5.14 a) Cross-sectional SEM image of a pouch cell of CuGF/Gr||NCM/ALD protected NiPGF and b-e) corresponding EDX mapping images of the mixture, Ni, Mn and Cu. f) Dynamic flexibility test for the pouch cell of CuGF/Gr||NCM/ALD protected NiPGF. Dynamic means that batteries was charged or discharged during the bending process. The total bending cycles are 750 times and the bending radius is 5 mm.

5.4 Conclusions

In summary, a high voltage and flexible current collector, NiPGF is prepared for extending applications of high-energy cathode materials. NiPGF/NCM electrodes (cut-off voltage of 4.4 V vs. Li/Li⁺) exhibit electrochemical performance similar to those using Al foils, indicating that NiPGF is highly stable at high potential. After illustrating the failure mechanism of NiPGF-based full cell, the ALD method is introduced to perfect the performance of the battery further. Finally, an energy-dense and highly flexible full cell is prepared by pairing it with CuGF/Gr anode. It could operate stably for more than 400 charge/discharge cycles with 82.6% capacity retention after 200 cycles. Also, it provides stable output power during a rigorous bending state with a bending radius of 5 mm.

Chapter 6. Ultrathin and Superlight Polyethylene Terephthalate (PET) Fabrics-based Current Collectors for High-energy Flexible Li-ion Battery

In this chapter, a high-performance flexible Li-ion battery (FLB) is developed by using polymer fabrics-based current collectors. Ultrathin and superlight polyethylene terephthalate (PET) fabrics possess high mechanical strength and excellent deformability, which are derived from the intrinsic property of PET and the woven structure of the fabrics. With the help of the polymer-assisted metal deposition (PAMD) method, metal-coated PET fabrics (MPETs) manifest a comprehensive property combining low cost, lightweight, high strength, outstanding mechanical durability, and high conductivity. Although PET is unstable on the anode side, additional electroplating is adopted to perfect the metal layer for fully covering the substrate. The related reaction and protection mechanisms are carefully investigated. Finally, the full cell using MPETs exhibit stable cycle performance with a high energy density of 207 Wh kg^{-1} , 17% higher than the commercial counterpart (177 Wh kg^{-1}). The flexibility is evaluated by two modes: segregated mode and synchronous mode. MPET-based pouch cells can operate normally after bending at an extremely low bending radius of 1 mm. Stable voltage output without drastic fluctuations (lower than 0.02 V) is also observed for the pouch cell under continuous bending at a bending radius of 3 mm.

6.1 Introduction

Li-ion batteries (LIBs) have become the most important energy storage device in our daily life although only 30-year techniques was developed.^{10, 28, 205} In an unprecedented period of rapid progress in flexible electronics, the demand for FLB makes more researchers work on it.^{215, 216} The major challenge is that the rigid components in conventional LIBs can not withstand large or long-term deformations.^{206, 207} The flexibility of a planar device depends on two parameters, the device's thickness and the intrinsic property of the material.³⁸ The essential requirement on the material is possessing a failing strain larger than 5%,^{17, 92} for which conventional current collectors, Cu and Al foils are not satisfied. In addition, these metal foils have a fatal defect that the mechanical durability is inferior.

Considering that the above analysis is based on the configuration of conventional LIB with a planer structure, scientists tried to design special structures to control the distribution of stress and strain within the whole battery.^{48, 115-119} Usually, in a typical structure, rigid segments that store the energy are protected by soft segments which buffer the external stress. However, these soft segments increase the proportions of the inactive materials, leading to a decrease in the energy density of the battery. Also, FLBs with designed structure always showed limited flexibility, for example, the reported spin-like battery⁵⁰ can be only bent in one direction. Another direct and efficient strategy is replacing metal foils with other soft materials. Among these, carbon nanotubes (CNTs) and graphene or other carbonaceous material display excellent electrical and mechanical performances.^{57, 58} However, carbonaceous materials can not be used as current collectors for those anodes with cut-off voltage lower than 0.9 V

because of the irreversible electrochemical reaction between Li^+ and carbonaceous materials.²⁰⁷ Moreover, the preparations of carbonaceous material are usually complex and expensive.

Alternatively, textile-based current collectors are more promising in future FLB developments. As well known for us, textiles have excellent mechanical performance, including strength, deformability, and long-term durability, which originate from the well-designed three-dimensional (3D) structure.^{22, 141} When using textile-based current collectors, the hierarchical structure also outperforms the planer foil in two aspects: 1. higher adhesion between the current collectors and active materials composite layer; 2. better electrolyte infiltration and thus shorter diffusion length for Li^+ . Our groups have made much effort into the development of the textile-based FLBs, however, either the fabrics are heavy and thick (e.g., carbon cloth¹⁹⁹) or the substrate is intrinsically rigid (e.g., glass-fiber fabrics²¹⁷).

Herein, we propose an ultrathin and superlight PET fabrics-based current collector for improved energy density. PET fabrics, with a famous trade name of Dacron, are commonly used fabrics with advantages of low cost, high strength and resilience. High-performance PET-based current collectors are prepared by combining these merits with the PAMD method. MPETs present great potential in high-energy FLBs: 1. MPET-based electrodes show comparable rate and cyclic performances to ones using metal foils while essentially cutting the current collectors' weight; 2. MPET-based full cell exhibit excellent flexibility in both the segregated and synchronous modes.

6.2 Experimental Part

6.2.1 Preparation of MPETs

MPETs were obtained by depositing Cu or Ni/P composite onto the PET fabrics through the PAMD method. Commercial PET fabrics with a thickness of 12 μm were chosen as the substrate, and PET pre-treatment is the same as the aforementioned process for glass-fiber fabrics in **Chapter 4.2.1**. Details of the subsequent electroless deposition (ELD) of Cu, Ni and Ni/P are also described.

The Cu-coated PET fabric is named CuPET; The Ni-coated PET fabric is named NiPET; and the Ni/P-coated PET fabric is named NiPPET.

6.2.2 Additional electroplating of Cu

As the PET is unstable at the anode side, a denser Cu layer is needed by additional electroplating. It was conducted using CuPET as the working electrode and Cu foil as the counter electrode in a commercial Cu electroplating solution at a current density of 0.5 mA cm^{-2} with different plating time. The resultant fabric is named ECuPET.

6.2.3 Atomic layer deposition (ALD) on CuPET

ALD method was also attempted to protect the PET substrate. Three sequences of the ALD process were applied, and they are named ALD1, ALD2 and ALD3 (Figure 6.1). In ALD1 and ALD2 routes, Al_2O_3 is deposited onto the CuPET/Gr electrode. The difference is that the edge of samples produced by ALD2 is also covered with Al_2O_3 but samples of ALD1 are not. In ALD3, the original PET substrate was coated with Al_2O_3 directly.

The specific ALD process was conducted at 80 °C in a thermal ALD system (Savannah, Veeco), and the deposition thickness of every cycle in this condition is 0.75 Å. Samples with different routes and deposition cycles were named ALDx-yy (x=1, 2, 3 and yy indicates the deposition cycles). For example, ALD1-20 is the sample of CuPET treated with 20 ALD cycles in route 1.

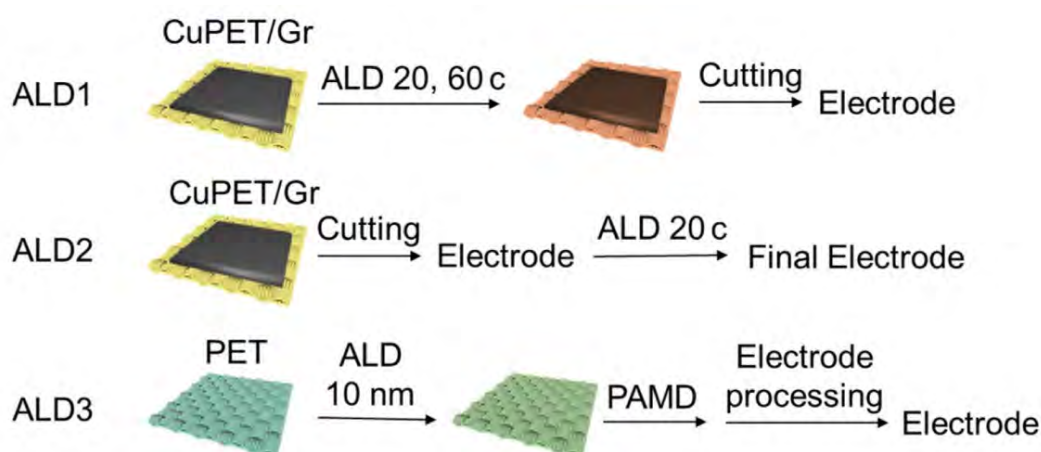


Figure 6.1 Schematic of different routes for ALD processes.

6.2.4 Cell assembly

The preparation details of electrodes and cell assembly can be found in **Chapter 4.2.2**.

6.2.5 Characterization

Morphology observations were conducted in a Scanning Electron Microscope (SEM, Tescan VEGA3). Mechanical performances of current collectors were tested by a universal testing machine (Instron 5566, USA). The electrical properties of current collectors are characterized by a source meter (Keithley 2400, USA). Battery performances were obtained by a battery test system (BTS 3000, Neware, China). Linear scanning voltammetry (LSV) and cyclic voltammetry (CV) were carried out by using an

electrochemical workstation (Biologic, France). FTIR spectra in the range of 4000 cm^{-1} to 650 cm^{-1} were recorded by PerkinElmer FT-IR Spectrum 100 equipped with an attenuated total reflection (ATR) accessory. Detailed information can be referred to **Chapter 3**.

6.3 Results and Discussion

6.3.1 Fabrication of MPETs and Basic Performances

PET fabrics with only $12\text{ }\mu\text{m}$ and 1.2 mg cm^{-2} were used in this work to fabricate the ultrathin and superlight current collectors. As shown in Figure 6.2a, MPETs are manufactured by the PAMD method. Cu and Ni/P composite were applied as coating materials in the anode and the cathode side. To better improve the stability of the current collector in the anode, CuPET was then electroplated with more Cu and the resultant sample is named ECuPET. The high-energy cathode material of lithium nickel cobalt manganese (NCM) and stable anode material graphite (Gr) were then coated onto the current collectors by the blade-coating method. Finally, a high-energy flexible battery can be assembled by pairing these MPET-based electrodes.

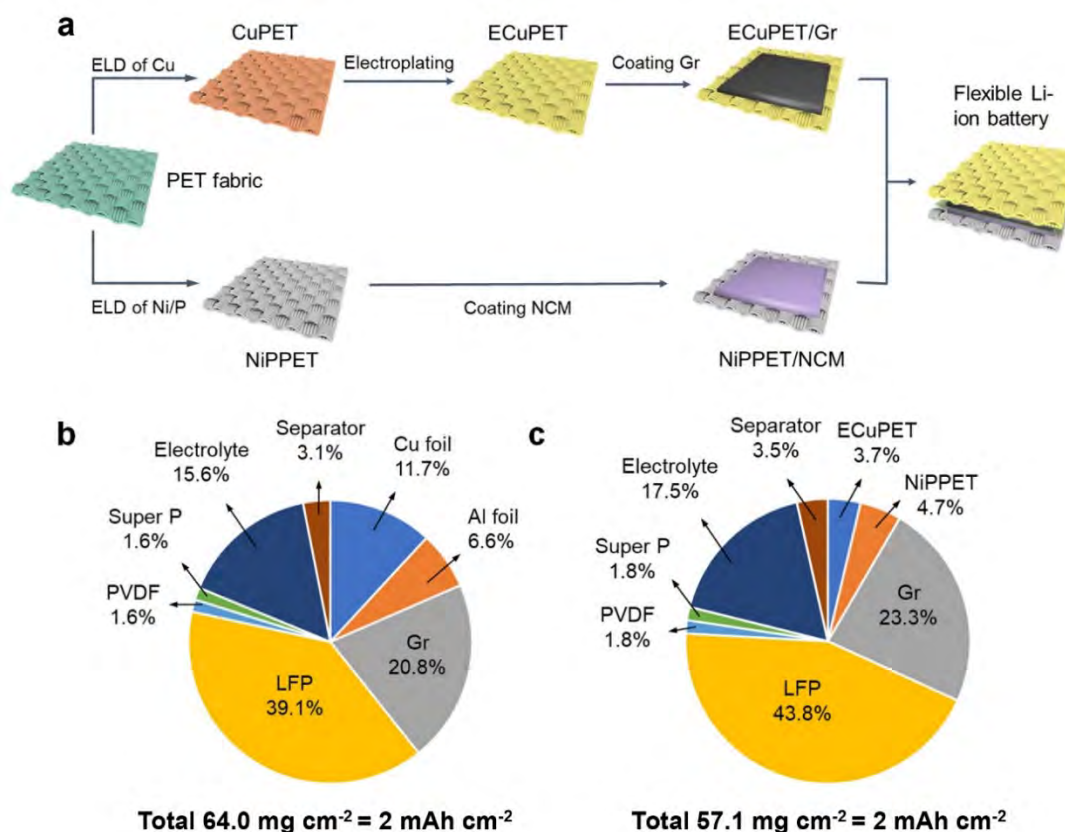


Figure 6.2 a) Schematic fabrication process of MPETs, MPET-based electrodes and flexible full cell. Pie chart of weight ratio in a battery using a) metal foils and b) MPETs with an areal capacity of 2 mAh cm⁻².

The active materials are electrochemically active and afford the function of storing energy so that they weigh major weight proportions of a battery. For example, in a commercial LIB with an areal capacity of 2 mAh cm⁻², Lithium iron phosphate (LFP) and Gr share ~60 wt% of the whole cell (Figure 6.2b, detailed information is listed in Table 6.1). But we notice that the total weight ratio of current collectors is very high to 20 wt% in this battery. In sharp contrast, ECuPET and NiPPET only share 3.7 wt% and 4.7 wt% of the whole battery, resulting in 10.8% of decrease in weight. Theoretically, an improvement of 12.1% for the gravimetric energy density can be realized by just replacing the metal foils of MPETs. Considering that the improvement of energy density

for LIBs is only 3~5% every year, MPETs are very promising current collectors for practical FLBs.

Table 6.1 Comparison of weights and fractions of components in a metal foil-based battery and an MPET-based battery.

	Metal foil-based battery		MPET-based battery	
	Weight (mg)	Fraction	Weight (mg)	Fraction (%)
Cu/ECuPET	7.5	11.7%	2.1	3.7%
Al/NiPPET	4.2	6.6%	2.7	4.7%
Gr	13.3	20.8%	13.3	23.3%
LFP	25	39.1%	25	43.8%
Electrolyte	10	15.6%	10	17.5%
Separator	2	3.1%	2	3.5%
Binder	1	1.6%	1	1.8%
Carbon black	1	1.6%	1	1.8%
Whole battery	64		57.1	

*The electrodes were double-side coated with active materials so the total capacity is 4 mAh and the areal capacity is 2 mAh cm⁻². The specific capacities of LFP and Gr are 160 mAh g⁻¹ and 320 mAh g⁻¹, respectively. The ratio of active material, binder and carbon black is 95:2.5:2.5 and the N/P ratio is 1.064.

By using the polymer as the intermediate layer, Cu and Ni/P composite are uniformly coated onto the PET fibers, resulting in highly conductive metal layers (Figure 6.3a and 6.3d). As the formation mechanism of the ELD process is the stack of numerous metal particles, both the ECuPET and NiPPET have a rough surface, which is beneficial to higher interfacial adhesion between the active material composite layer and the current collectors (Figure 6.3 b and 6.3e).

It should be mentioned that the additional electroplating makes the Cu particles grow larger but does not change the overall morphology. The cross-sectional view illustrates that the PET fibers are not perfect circles but show a flattened oval shape. It is attributed to the deformable property of the PET polymer (Figure 6.3c and 6.3f).

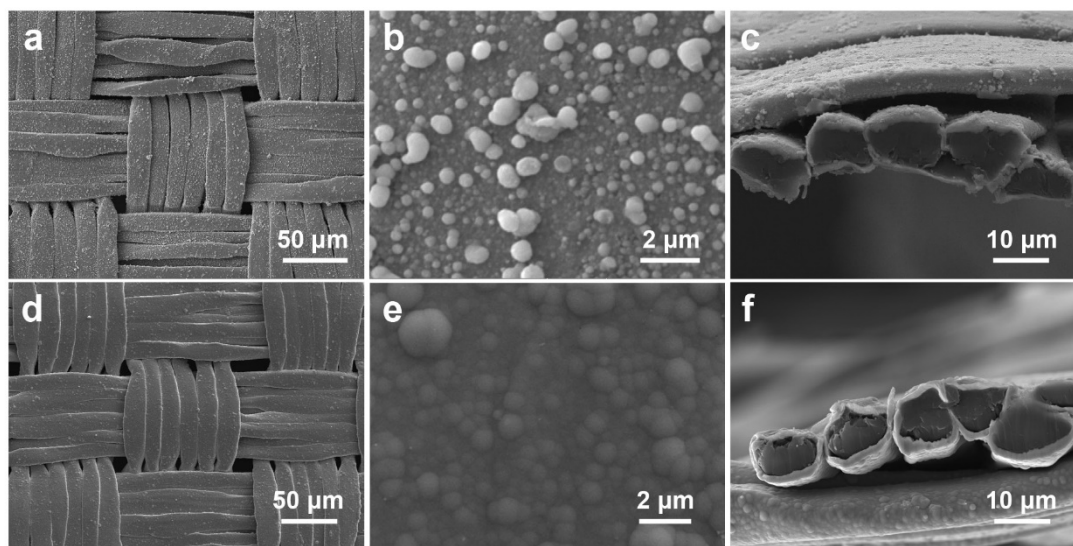


Figure 6.3 SEM images of ECU PET with a, b) top view and c) cross-sectional view, and Ni PET with d, e) top view and f) cross-sectional view.

Conductivity and areal density are two critical parameters for current collectors because the former decides the transportation ability of electrons and the latter influences the gravimetric energy density. After optimization of the balance between the weight and conductivity, the resultant ECU PET and Ni PET show areal densities of 2.1 and 2.7 mg cm⁻², much lighter than commercially used Cu foil and Al foil (Figure 6.4 and detailed information in Table 6.2). Simultaneously, MPETs have high conductivities of 9.4×10^4 and 5.8×10^3 S cm⁻¹, which are adequate for electron transportation. In addition, our MPETs show lower areal densities than MGFs, meaning that a higher energy density can be realized for the MPET-based batteries.

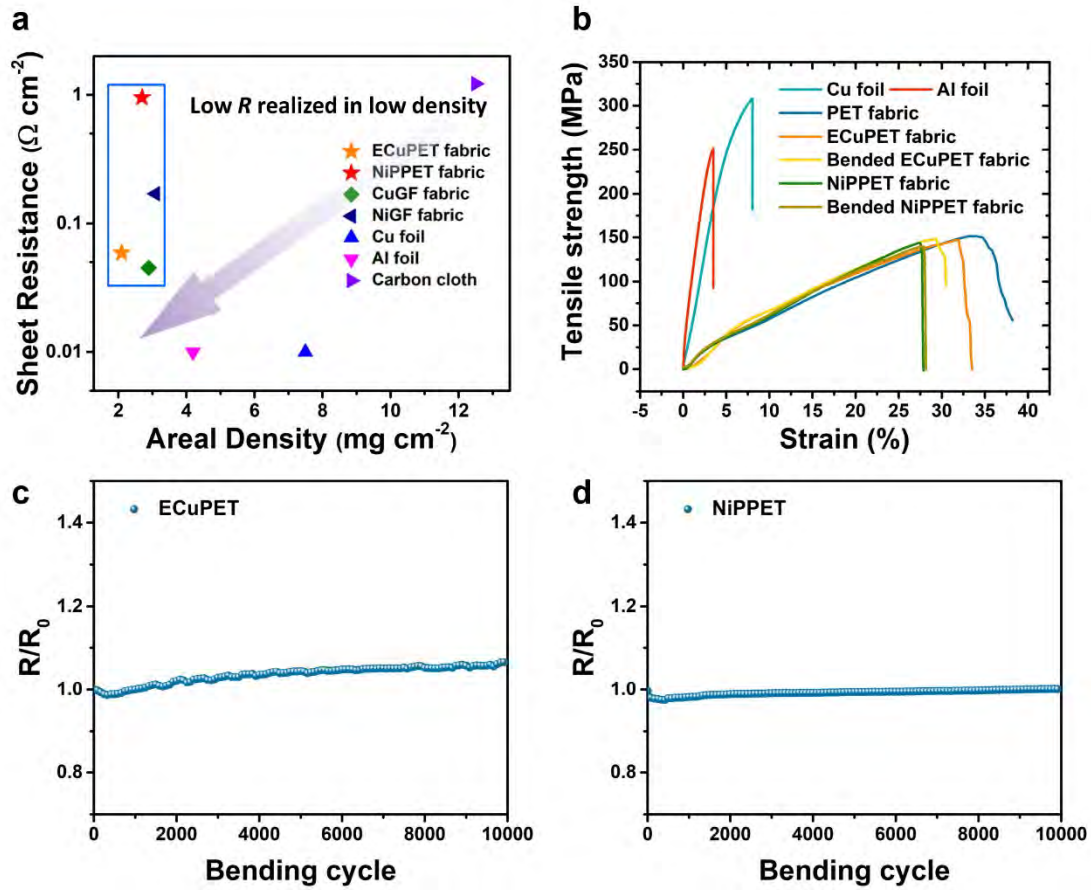


Figure 6.4 a) Comparison of conductivity and areal density between different current collectors. b) Typical stress-strain curves for metal foils and MPETs. Electrical conductivity variation as a function of bending cycles for c) ECU PET and d) NiPPET at the bending radius of 2 mm.

Mechanical strength is one of the critical properties of a qualified current collector. Generally, 100 MPa is the least limit to withstand the tension stress during roll-to-roll manufacturing. Both ECU PET and NiPPET exhibit mechanical strengths of ~ 150 MPa and high breaking strains of $\sim 30\%$ (Figure 6.3b). Although Al foil and Cu foil have high strengths they are easily fractured because of low elongation at break (lower than 10%). After 10,000 bending cycles at the bending radius of 2 mm, the mechanical properties of ECU PET and NiPPET remain virtually unchanged (Figure 6.4b). With the robust adhesion between the metal layer and the fabrics, the variations of resistance for

ECuPET and NiPPET are lower than 5% after bending cycles (Figure 6.4c and d).

Table 6.2 Comparison of conductivity and areal density between different current collectors

Materials	Mass Density (mg cm ⁻²)	Resistance (Ω cm ⁻²)	Conductivity (S cm ⁻¹)
PET	1.2	NA	NA
ECuPET	2.1	0.059	9.4×10^4
NiPPET	2.7	0.95	5.8×10^3
GF	2.0	NA	NA
CuGF	2.9	0.046	1.1×10^5
NiGF	3.1	0.17	3×10^4
Cu foil	7.5	< 0.01	6×10^5
Al foil	4.2	<0.01	$\sim 10^5$

*GF, CuGF and NiGF are glass fiber fabrics, Cu-coated galss fiber fabrics and Ni-coated glass fiber fabrics.

6.3.2 PET-derived Side Reactions and Protection of Substrate

At first, the cycle performance of the CuPET/Gr electrode is measured, however, we find that CuPET/Gr has lower coulombic efficiencies (CEs) than those of the Cu/Gr electrode (Figure 6.5a). It is speculated that some side reactions occur for CuPET when the electrode cycles between 0.005-2V (vs. Li/Li⁺). CE of the CuPET/Gr electrode rises with cycles but can not reach the Cu/Gr electrode level, indicating that the side reaction exists persistently in CuPET/Gr-based cells with gradually decreased amounts. Surprisingly, The ECuPET/Gr electrode shows comparable CEs to those of the Cu/Gr electrode and the same trend of the change for CEs. It means that additional electroplating Cu can prevent the side reaction effectively. The electroplating time was

monitored to identify the appropriate condition at electroplating current density of 0.5 mA cm^{-2} (Figure 6.5b). With 15-min-electroplating, the CEs are improved but still lower than those of the Cu/Gr electrode. The samples with 30 min and 120 min electroplating time have identical CEs to each other, demonstrating that 30 min electroplating (equal to 0.3 mg cm^{-2} Cu) is enough to fully protect the CuPET.

As a result of the difference in CEs, the cyclic performance of the full cell using CuPET as the anode current collector is inferior with lower CEs, compared to the metal foil-based full cell. By using the ECuPET, the capacity retention increases a lot from 69.5% to 82.6% after 100 cycles. Higher CEs of the ECuPET-based full cell mean that the side reaction is prevented, leading to less Li loss in every charge-discharge cycle.

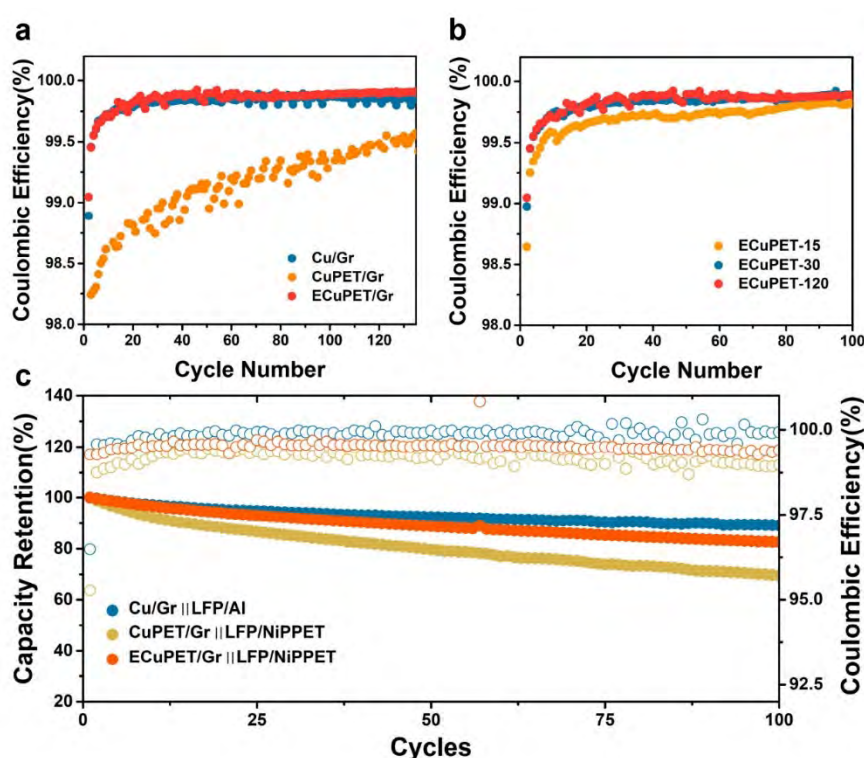


Figure 6.5 a) Coulombic efficiencies of Cu/Gr, CuPET/Gr and ECuPET/Gr electrodes. b) Coulombic efficiencies of ECuPET/Gr electrodes with different electroplating time of 15, 30, and 120 min. c) Cyclic performance of full cells of Cu/Gr||LFP/Al, CuPET/Gr||LFP/NiPPET, and ECuPET/Gr||LFP/NiPPET.

To figure out the side reaction introduced by CuPET, the half cells were disassembled, then the Cu and the active material of the electrodes were removed to test the substrate by FTIR. The peak at 1710 cm^{-1} denotes the -COO- groups on the PET chains, and the location at 1410 cm^{-1} is the peak of C-C stretching on the benzene ring. For the CuPET operated for 200 cycles, the peak at 1710 cm^{-1} is split into two peaks with the shoulder peak located at 1670 cm^{-1} , which indicates the generation of the -C=O- group (Figure 6.6a). In addition, the intensity of the benzene ring C-C peak increases a lot compared to other peaks, implying the production of terephthalic acid-derived chemicals because the monomer has a higher intensity in 1410 cm^{-1} than the polymer. After 500 cycles, FTIR signals of the cycled CuPET sample are very weak. The peak of 1710 cm^{-1} disappears and entirely shifts to 1670 cm^{-1} . It is worth mentioning that the CuPET current collector is too fragile to be picked up in an integrated piece. In other words, the CuPET has lost its original mechanical performance thoroughly. Combined with the FTIR results, we conclude that the side reaction for PET continues during the battery cycles and finally PET is degraded completely. Fortunately, ECuPET operated for 500 cycles exhibits a typical curve the same as the original PET, demonstrating that the additional electroplating Cu effectively protects the PET substrate from side reactions.

The type of side reaction for PET in the battery should be clarified. The reactivity between the PET and Li metal is first revealed. We put PET, CuPET and ECuPET into the coin cell, then Li foil was placed on the top of them. By adding the same electrolyte, the cells were sealed to simulate the battery environment but without the electrical field. The results show that pure PET is stable with Li metal in the electrolyte, evidenced by the almost identical FTIR curves for the original PET and PET placed with Li for a

month (Figure 6.6b). However, by plating with Cu, the degradation of CuPET can be detected in FTIR results. The split of the peak for C=O is apparent for the CuPET in contact with Li for 2 days, which is further deteriorated after 10 days. A simple conclusion is that Cu acts as a catalyst or an electron mediator between the PET and Li, speeding up the side reaction. Even with the protection of additional electroplating, the ECuPET sample also presents a shoulder peak at 1670 cm^{-1} after 10 days, meaning that the reaction between PET and Li is very quick and strong.

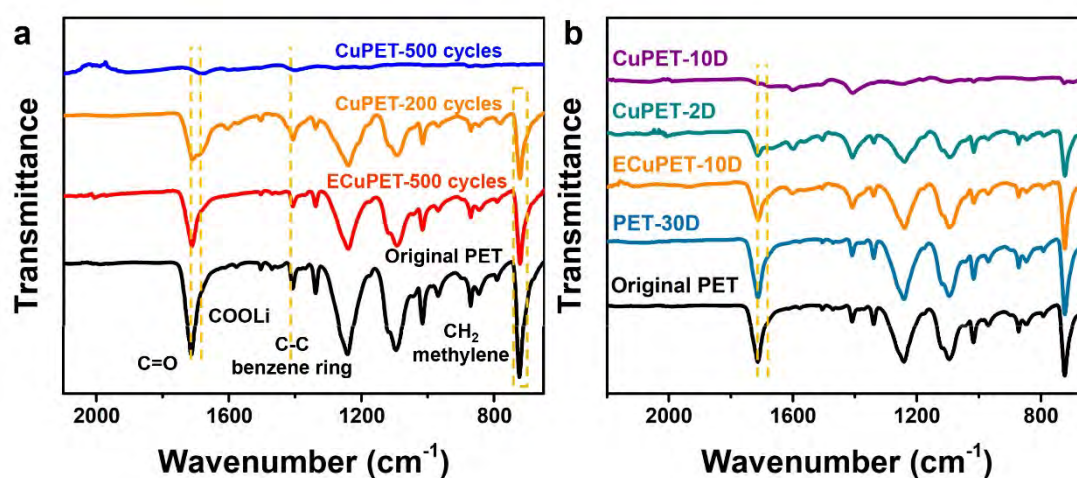


Figure 6.6 a) FTIR results of CuPET and ECuPET detached from the cycled batteries. b) FTIR results of PET, CuPET and ECuPET in contact with Li in electrolyte after different days.

The reaction between the PET and Li^+ was investigated by setting the current collectors at 0 V vs Li/Li^+ . The condition was determined considering the working range of the graphite electrode and the prevention of Li deposition which needs a negative voltage to overcome the overpotential. After only one day, a shoulder peak at 1670 cm^{-1} appears for CuPET, with an increased intensity of the C-C peak on the benzene ring (Figure 6.7). It means that the PET substrate does not only react with Li metal but also the Li ions. After just 5 days, the -COO- peak is almost vanished and the peaks of the derivatives are

located at the range of 1640-1680 cm^{-1} . Actually, the CuPET sample set at 0 V for 6 days loses its free-standing property and can not be tested anymore. By sharp contrast, ECuPET mainly maintains its original chemical structure in the first 7 days (Figure 6.7b). After a long-term test of 30 days, apparent degradation peaks can be found for the ECuPET. Continuous staying at 0 V is a harsh condition for a current collector because the accumulated time of a current collector staying at 0 V counts deficient proportion for a LIBs. From this point, ECuPET has shown outstanding stability on the anode side although the degradation of PET is not totally prevented,.

As the change for the C=O peak is the most conspicuous, we use the intensity ratio between the peak at 1710 cm^{-1} to peaks in the range of 1640-1680 cm^{-1} ($I_{1710}/I_{1640-1680}$) to quantitatively estimate the degradation level of the substrate (Figure 6.7c). A linear decrease of $I_{1710}/I_{1640-1680}$ is observed for CuPET, which quickly declines to 0.2 after only 5 days. On the contrary, the intensity ratio for ECuPET fluctuates from 2.3-2.7 in the first week. It seems that the electroplated Cu effectively hinders the contact between the PET and Li^+ , thus limiting the side reaction to a great extent.

The higher stability of ECuPET can be demonstrated by the leak current density when the CuPET and ECuPET samples are set at 0 V vs. Li/Li^+ (Figure 6.7d). ECuPET shows a stable leak current during 30 days while CuPET presents much higher current densities with fluctuation. It is believed that the extra electron flow for the CuPET is attributed to the side reaction between PET and the electrolyte.

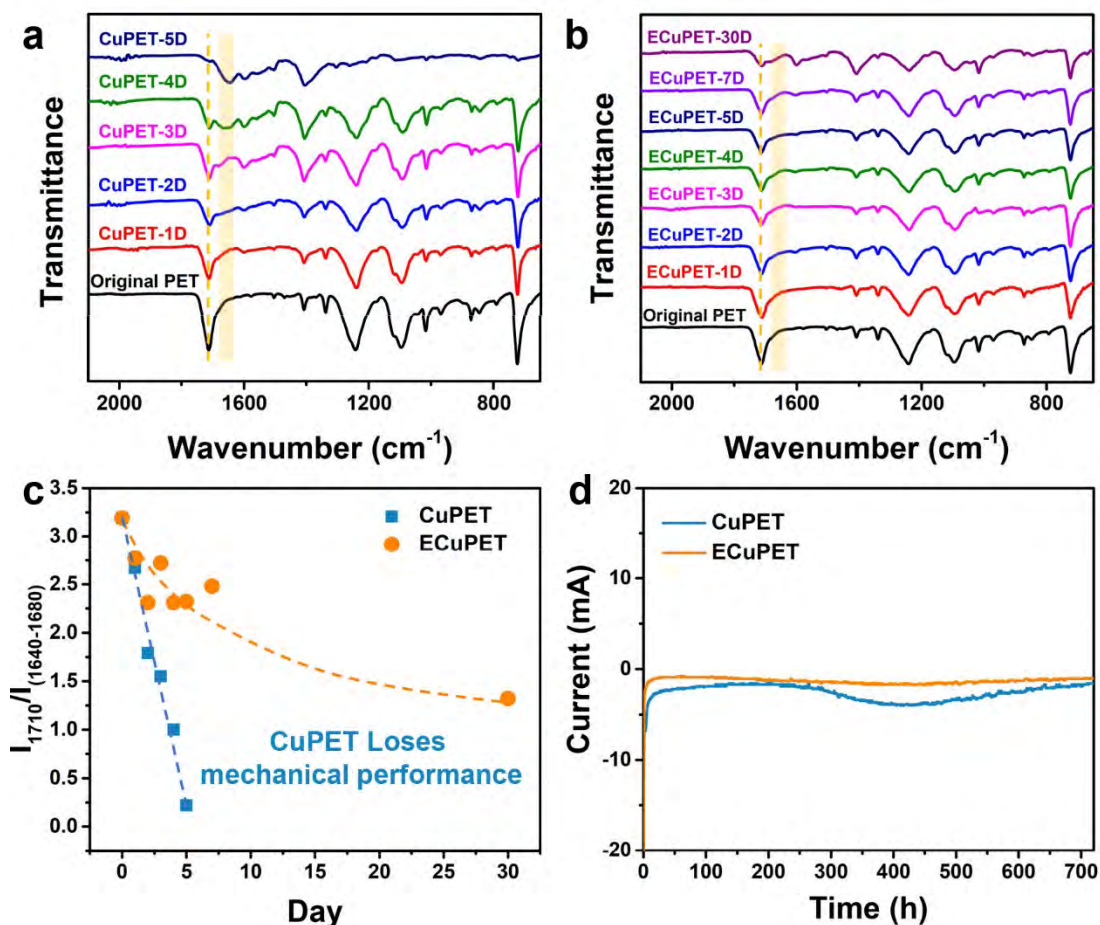


Figure 6.7 FTIR results of a) CuPET and b) ECuPET detached from the Li||CuPET cell set at 0 V (vs. Li/Li^+) for different days. c) The intensity ratio of the peak at 1710 cm^{-1} to peaks at the range of 1640-1680 cm^{-1} as a function of time for CuPET and ECuPET at the constant voltage at 0 V (vs. Li/Li^+). d) The current responses of CuPET and ECuPET when set as 0 V (vs. Li/Li^+).

The ALD method is adopted to protect the substrate and the Al_2O_3 layer was deposited onto pure PET, the CuPET, or the fabricated CuPET/Gr electrode (specific processes are shown in the Experiment Part). However, all the ALD-protected electrodes exhibit inferior capacities than the CuPET/Gr electrode (Figure 6.8a). Although the CEs are improved a little by the ALD protection, they still need to be higher to meet a qualified level (Figure 6.8b). Also, it can be seen that the change trends of CEs for these ALD-

protected electrodes are the same as the CuPET/Gr electrode. It illustrates that deposited Al_2O_3 can not stop the restrain the side reaction but just slow down the reaction rate. Theoretically, the Al_2O_3 -derived lithium aluminum compound allows enter of Li^+ but prevent the Li metal from the substrate. The unsucces of the protection by the ALD method proves again that the low CEs of CuPET originate from the side reaction between the PET substrate and Li^+ .

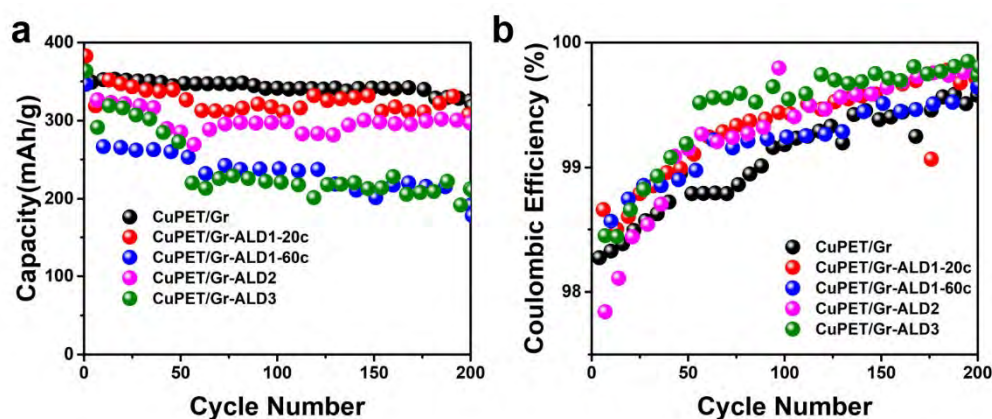


Figure 6.8 a) Cycle performance of ALD-protected CuPET/Gr electrodes and b) corresponding CEs during cycling.

A dense metal layer is believed to segregate the inner PET from the electrolyte so the degradation of CuPET must relate to the morphology of the deposited Cu by ELD method. In this regard, the process of ELD for Cu was monitored to see the potential cause of the leak for the electrolyte. The process starts with the nucleation of Cu, and then these Cu granules grow (Figure 6.9a and 6.9b). Some small granules form a connected layer like a “lawn”, and some big Cu particles are dispersed on the surface of the “lawn” (Figure 6.9c and 6.9d). Then these particles continuously grow up and finally form a whole layer that seems intact (Figure 6.9e-h). However, there may be cracks within the metal layer because the formation mechanism is the stack of Cu particles. The whole process is also schematically illustrated in Figure 6.9i. The space

between these stacked Cu particles allows the electrolyte to access the PET substrate, finally resulting in the degradation of the polymer. And the additional electroplating is like a repair process to fill these gaps so that ECuPET has excellent stability on the anode side.

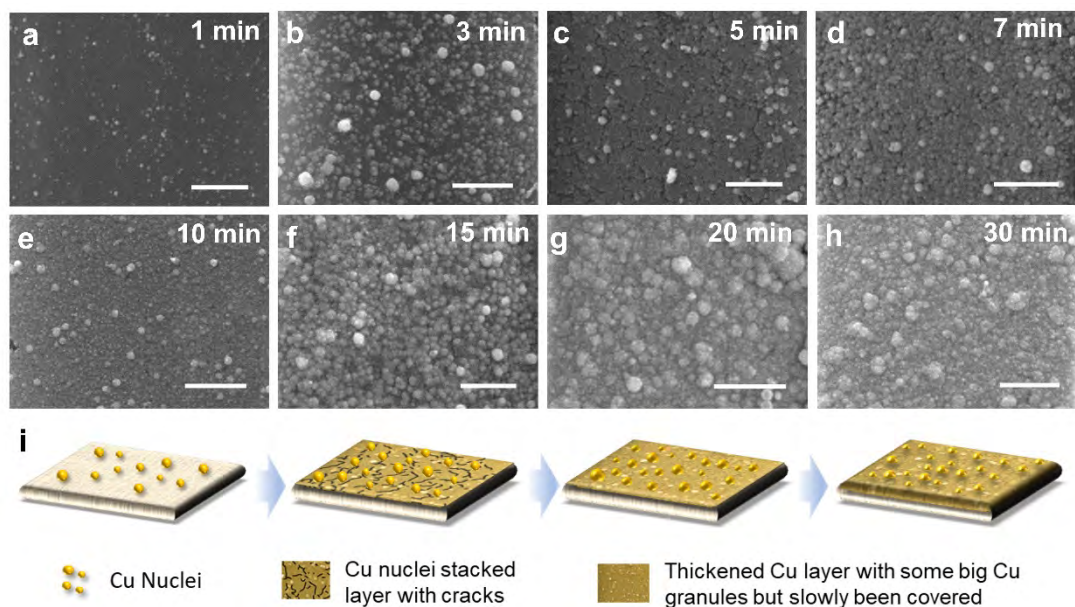


Figure 6.9 SEM images of morphology change of CuPET with ELD time of a) 1 min, b) 3 min, c) 5 min, d) 7 min, e) 10 min, f) 15 min, g) 20 min, and h) 30 min. And i) Schematic growth process of Cu layer in ELD. The scale bar is 2 μm .

To sum up, PET has reactivity with Li^+ under the electrical field. The side reaction between the PET and Li^+ is not reversible, thus leading to the continuous consumption of Li source, which is reflected by the lower CEs. As illustrated by Figure 6.10a, CuPET has the morphology feature of the Cu layer with some micro-holes which allows the penetration of electrolytes. In this case, electrons are transported through the Cu layer while the Li^+ can also access. Hence, PET decomposes into the aldehyde and alcohol derivatives of the terephthalic acid as well as glycol at high speed in the junction under a reductive driving force of the electrical field (Figure 6.10c). This phenomenon is largely

restrained by the electroplating of Cu as the micro-holes in the original Cu layer are filled by the electroplated Cu (Figure 6.10b). Although PET can still get electrons from the Cu layer, Li ions are segregated from the PET, leading to a higher stability of the ECuPET than the untreated CuPET.

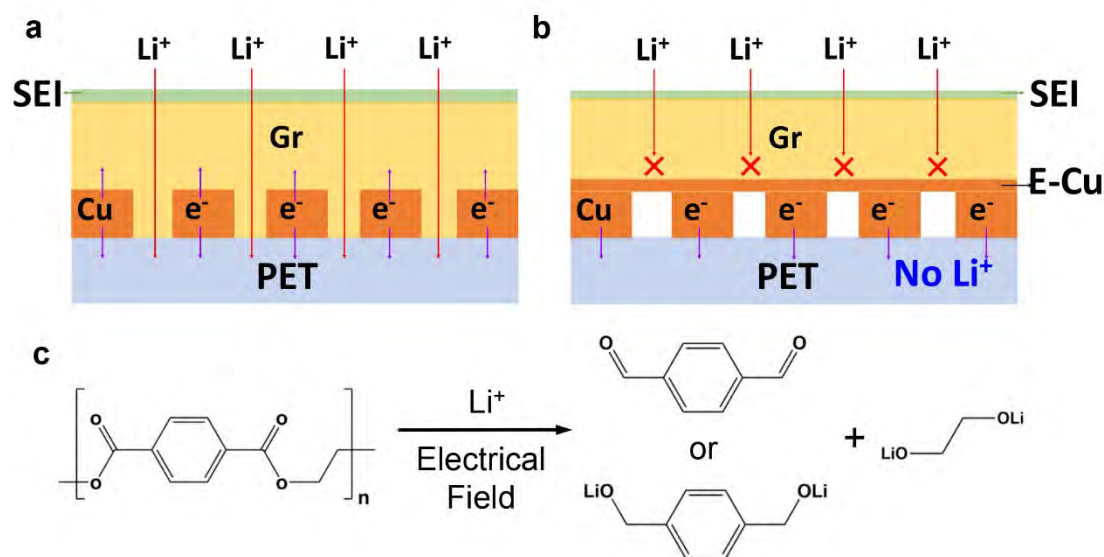


Figure 6.10 Schematic reaction mechanism and protection of PET substrate.

6.3.3 Electrochemical Performances of MPET-based Electrodes and Full Cells

The electrochemical performance of the ECuPET/Gr electrode was tested. As shown in Figure 6.11a, the ECuPET/Gr electrode has a similar rate capability to the Cu/Gr electrode, showing a high capacity of $\sim 350 \text{ mAh g}^{-1}$ at a rate of 0.5 C. For a practical application, the current collector's weight must also be considered. If we calculated the capacity based on the whole electrode including the current collector, the capacity of the ECuPET/Gr electrode is almost twice as large as that of the Cu/Gr electrode. It originates from the ultrathin and ultralight ECuPET substrate with areal density of 2.1

mg cm⁻², much lighter than the Cu foil (7.5 mg cm⁻²). In addition, the ECuPET/Gr has high cyclic stability during long-term tests. After 300 charge-discharge cycles, the capacity retention of the ECuPET/Gr electrode is 97.5%, comparable to that of the Cu/Gr electrode (Figure 6.11b).

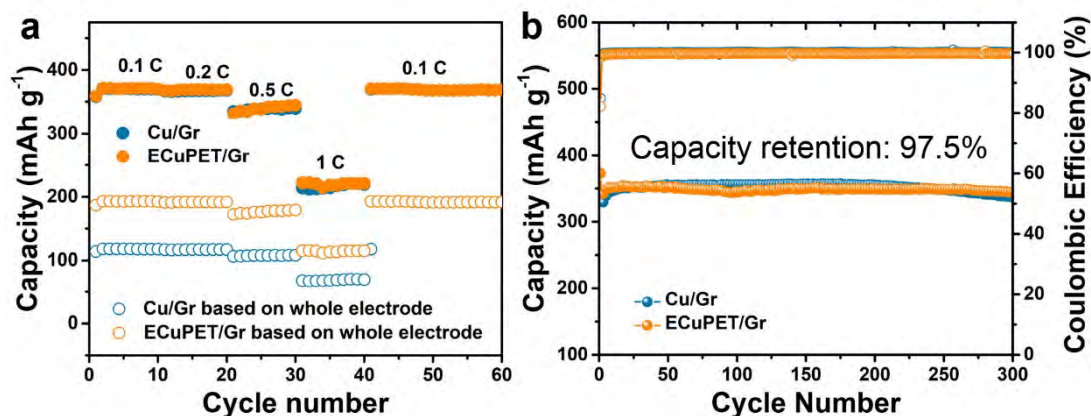


Figure 6.11 a) Rate of Cu/Gr and ECuPET/Gr electrodes. b) Cycle performances of Cu/Gr and ECuPET/Gr electrodes at the rate of 0.5 C. The areal capacity is 1.25 mAh cm⁻².

For the cathode side, Ni/P composite rather than Ni metal is adopted as the coating layer of the PET substrate because NiPPET shows much higher anodic stability than NiPET (Figure 6.12a). The onset anodic current starts at ~4.7 V vs. Li/Li⁺, which is adequate for most cathode materials. Cyclic test in the range of 3-4.5 V vs. Li/Li⁺ indicates that NiPPET has long-term stability in this range (Figure 6.12b). Compared to the commercial Al/NCM electrode, the rate and cycle performances of the NiPPET/NCM electrode are almost identical. It exhibits a high capacity of 174 mAh g⁻¹ at 1 C, around 86.5% of the capacity at 0.1 C (Figure 6.12c). Moreover, a capacity retention of 92.5% is achieved for the NiPPET/NCM electrode after 200 cycles (Figure 6.12d). These results demonstrate that the NiPPET is an outstanding current collector on the cathode side to support a high-performance full cell.

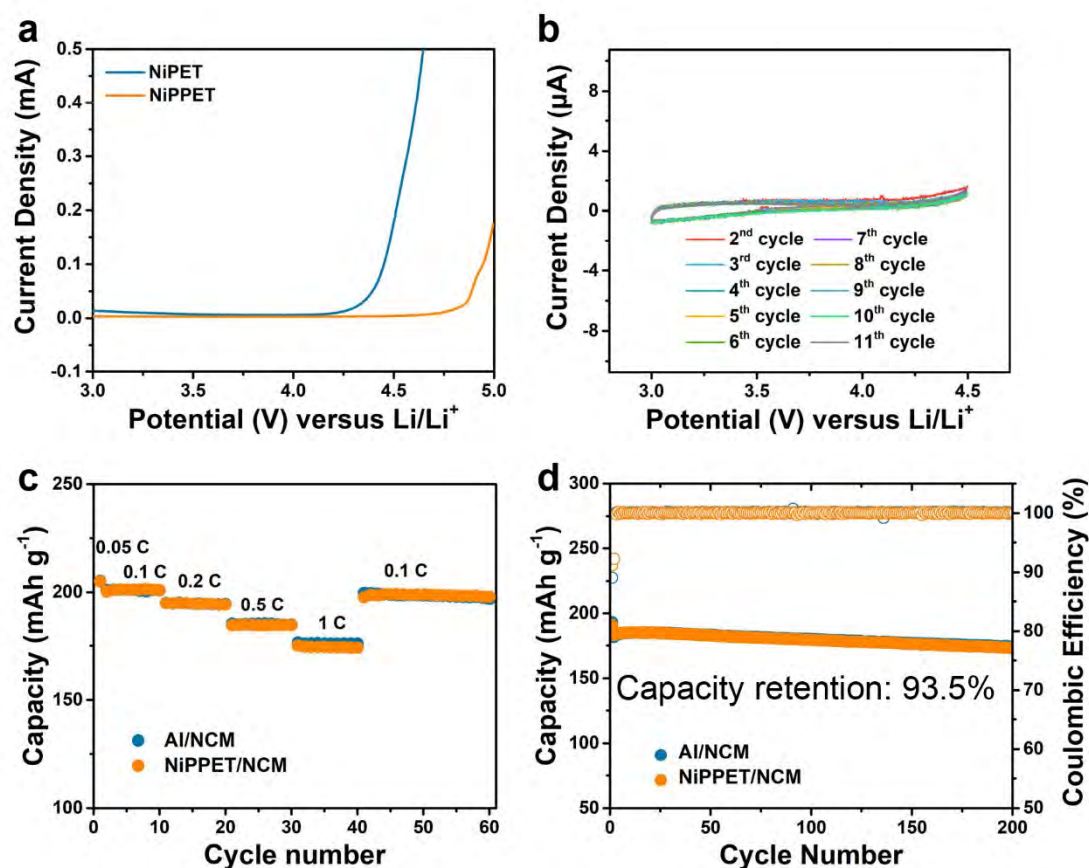


Figure 6.12 a) LSV curves of NiPET and NiPPET recorded at a scan rate of 0.5 mV s^{-1} in the range of 3 to 5 V vs Li/Li⁺. b) CV curves of NiPPET recorded at a scan rate of 0.5 mV s^{-1} in the range of 3 to 4.5 V vs Li/Li⁺. c) Rate and d) cycle performance of Al/NCM and NiPPET/NCM electrodes.

Motivated by the excellent electrochemical performances of the ECuPET/Gr electrode and the NiPPET/NCM electrode, we pair them together to assemble a full cell with an N/P ratio of ~ 1.1 . It exhibits similar cyclic stability to the full cell using metal foils, with a capacity retention of 88.3% after 200 charge-discharge cycles (Figure 6.13). Benefiting from the much lower areal densities of MPETs than metal foils, the full cell of ECuPET/Gr||NCM/NiPPET has a high gravimetric energy density of 220 Wh kg^{-1} , 17% higher than the full cell using metal foils (183 Wh kg^{-1}). Considering that there is much unoccupied space in PET fabrics, the equivalent thickness of MPET is calculated

to be 9.9 μm (the utilization ratio of unoccupied space is set as 60%). The total thickness of current collectors decreases from 23 μm (8 μm for Cu foil and 15 μm for Al foil) to 19.8 μm . As a result, the estimated volumetric energy density of the full cell is also improved by $\sim 2\%$. It is realized by just replacing the current collector without changing the electrochemical performance.

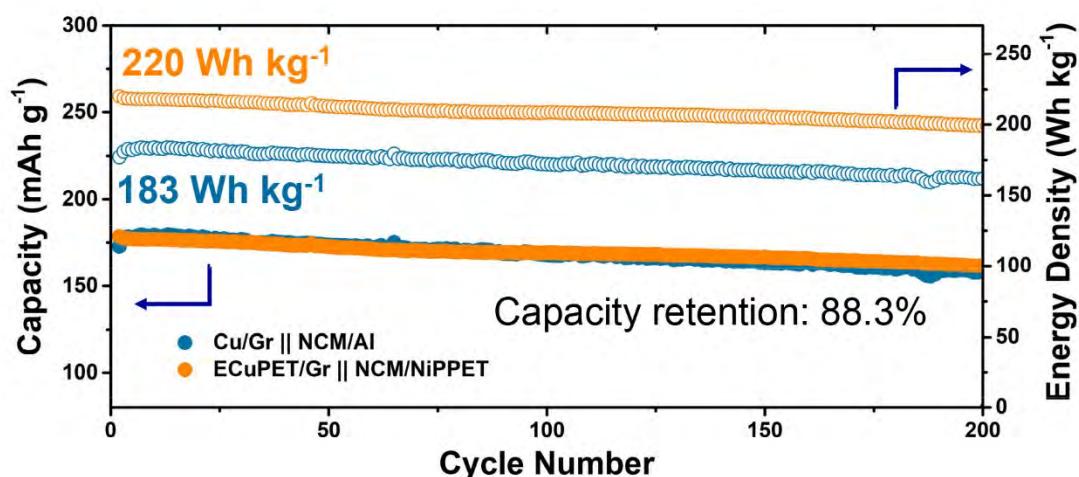


Figure 6.13 Cycle performance of the full cells of Cu/Gr||NCM/Al and ECuPET/Gr||NCM/NiPPET.

6.3.4 Flexibility of MPET-based Pouch Cells

PET is a kind of flexible and robust polymer. In addition to the well-designed textile structure, PET fabrics have excellent mechanical performance. The flexibility of the composite electrode layer is also revealed by Based on this advantage, the MPET-based pouch cell is believed to show good flexibility. Here, two kinds of test methods were conducted, segregated mode and synchronous mode, which depend on whether the bending process is simultaneous with the charge/discharge programs.

For the segregated-mode flexibility test, the pouch cell was bent at bending radii of 5 mm, 2mm and 1mm for 1500 cycles and then was folded for 500 cycles (Figure 6.14a).

The ECuPET/Gr||NCM/NiPPET pouch cell presents a high capacity retention of 88.4% after 1000 bending cycles, showing excellent mechanical robustness even under a harsh bending state with a bending radius of 2 mm. Under a lower bending radius of 1 mm, the decay of capacity speeds up, resulting in a capacity retention of 78.4% after 1500 bending cycles. Surprisingly, our MPET-based pouch cell is reliable at the first 200 cycles of the folding process, showing a capacity retention of 72.1%. However, after follow-up 300 cycles of folding, the capacity sharply declines from 1.35 mAh cm⁻² to 0.97 mAh cm⁻², which implies the severe deterioration of the electrodes within the pouch cell. The corresponding galvanostatic charge/discharge (GCD) curves after bending or folding manifest typical features of NCM materials but with higher overpotentials (Figure 6.14b).

EIS results of the ECuPET/Gr||NCM/NiPPET pouch cell at the flat state and after different cycles of bending and folding were recorded. Two semicircles that correlate to the R_{int} (internal resistance) and R_{ct} (the resistance derived from charge transfer) appear for all the samples. After bending at 5 mm and 2 mm, the R_{int} increases slightly with a stable R_{ct} compared to the flat state (Figure 6.14c-e). The slight increase in contact resistance may be triggered by the partial detachment of active materials on the current collector. Bending at 1 mm for 500 cycles promotes simultaneous rises on R_{int} and R_{ct} , thus leading to higher overpotential and fast capacity decay (Figure 6.14f). The slower kinetics of charge transfer is mainly originated from the damage to the electrodes. By abusing the pouch cell in the folding process, the R_{int} and R_{ct} increase rapidly, resulting in a sharp decline in capacity retention (Figure 6.14g and 6.14h).

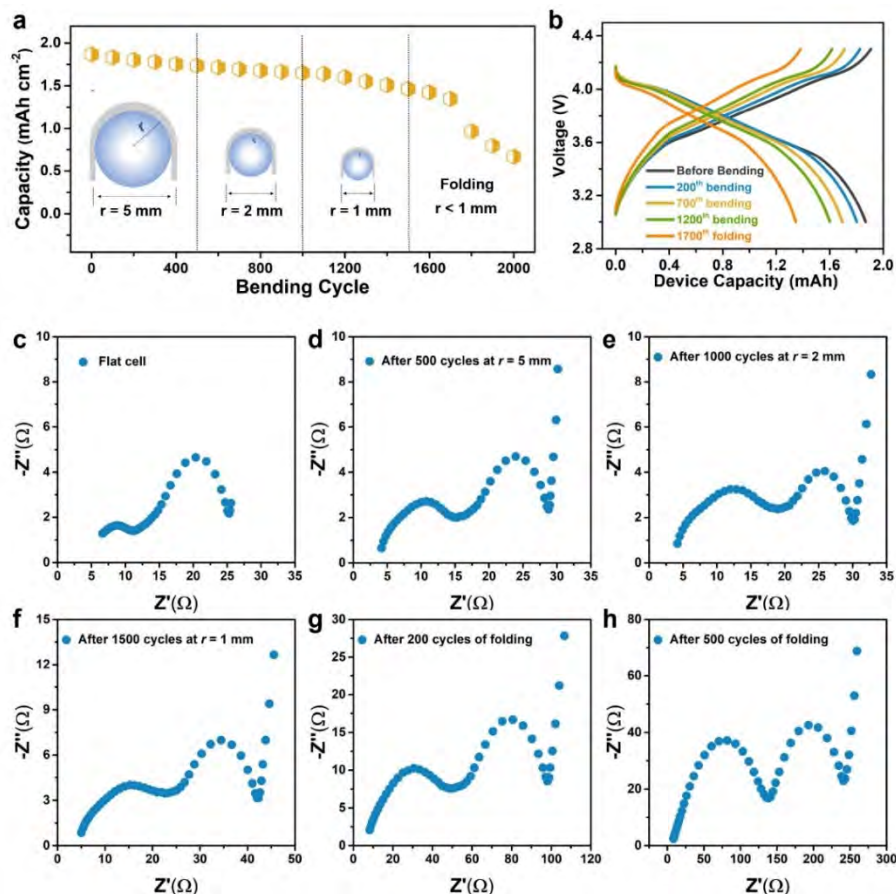


Figure 6.14 a) Areal capacity change of the ECuPET/Gr||NCM/NiPPET pouch cell after 1500 bending cycles at radii of 5 mm, 2 mm and 1 mm, and 500 folding cycles. b) Corresponding GCD curves of the pouch cell after bending and folding cycles. EIS results of the ECuPET/Gr||NCM/NiPPET pouch cell c) at the flat state, and after d) 500 bending cycles at $r = 5$ mm, e) 1000 bending cycles at $r = 2$ mm, f) 1500 bending cycles at $r = 1$ mm, g) 200 folding cycles and h) 500 folding cycles.

Considering that the synchronous-mode test is more rigorous than the segregated-mode test, the bending radii were chosen as 7mm, 5mm and 3mm. The ECuPET/Gr||NCM/NiPPET pouch cell shows 1.76, 1.66 and 1.50 mAh cm⁻² at bending radii of 7mm, 5mm and 3mm, respectively (Figure 6.15a). Compared to the 1.73 mAh cm⁻² at the flat state, the pouch cell displays excellent flexibility and durability during continuous flexing. The potential fluctuations for pouch cell bending at 5 mm and 3

mm are minimal, as shown in the enlarged GCD curves (Figure 6.15b-d and 6.15f-h). The undulation of the potential is more pronounced when the pouch is bending at 3 mm but is still acceptable for a working battery. In addition, it can be seen that the fluctuations on the charge curve are more minor than those on the discharge curve. These results demonstrate that our MPET-based flexible battery has high output stability during harsh flexing tests.

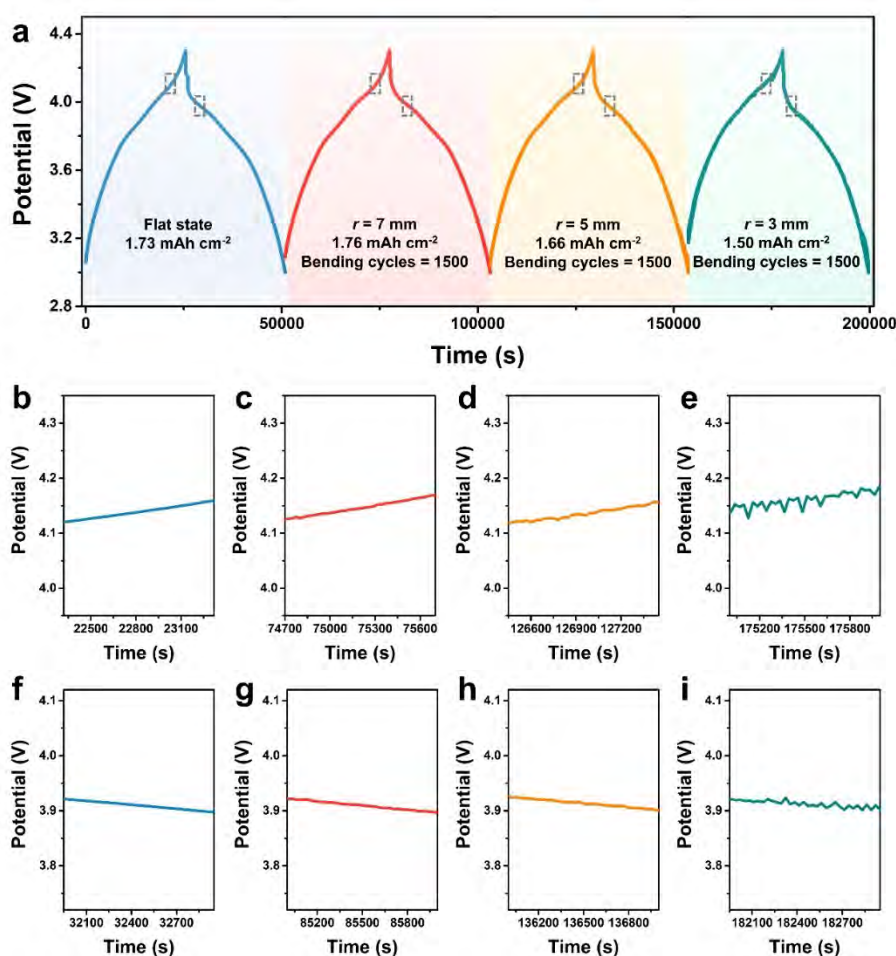


Figure 6.15 a) GCD curves of ECuPET/Gr||NCM/NiPPET pouch cell at the flat state and during continuous bending process at bending radii of 7 mm, 5 mm and 3 mm. Localized enlarged curves in the charging process of the pouch cell with b) flat state and bending process at radii of c) 7 mm, d) 5 mm, and e) 3 mm. Localized enlarged curves in the discharge process of the pouch cell with f) flat state and bending process at radii of g) 7 mm, h) 5 mm, and i) 3 mm.

6.4 Conclusions

In summary, we prepare a highly flexible and ultralight current collector based on PET fabrics. By evaluating the MPET-based electrodes, we find that PET is unstable on the anode side and the degradation process of PET is monitored. The additional electroplating acts as a repair process to fully cover the PET substrate, successfully separating it from the electrolyte. The full cell using MPETs outperforms the commercial counterpart in energy density, showing a 17% improvement from 177 to 207 Wh kg⁻¹. By inheriting the excellent mechanical property of PET fabrics, the pouch cell is highly flexible and durable. After thousands of bending processes at radii of 5 mm, 2 mm, and even 1 mm, the cell keeps high retention of ~80%. Moreover, it displays a discharging areal capacity of 1.5 mAh cm⁻² under a synchronous-mode bending process at a small radius of 3 mm, compared to 1.73 mAh cm⁻², the discharging areal capacity of the flat state. These results indicate that MPET-based FLBs are reliable in extreme and long-term continuous bending states.

Chapter 7 Conclusions and Suggestions for Future Research

7.1 Conclusions

In this thesis, we develop superlight fabric-based current collectors for high-energy flexible Li-ion batteries (FLBs). By applying the polymer-assisted metal deposition (PAMD) method, highly conductive and mechanically durable metal layers with excellent interfacial adhesive force are prepared through the polymer buffering interlayer. The electroless deposition (ELD) process is suitable for roll-to-roll manufacturing, thus the production of metal-coated fabrics (MFs) can be easily scaled up. These MFs display comprehensive properties, combined with high conductivity, high electrochemical stability, and outstanding mechanical performances. Without changing the electrochemical performances of the electrodes, replacing the conventional metal foils with MFs demonstrates improvements in energy density by up to 18%, which is attributed to the much lower areal densities of these developed MFs.

In Chapter 4, commercial glass-fiber fabrics (GFs) with a thickness of 20- μm are adopted as the substrate in consideration of the electrochemical stability and mechanical requirements. These metal-coated GFs (MGFs) only weigh 2.9-3.2 mg cm^{-2} , accounting for ~40% of the Cu foil (7.5 mg cm^{-2}). It leads to 9-18% improvements in energy density for different cathode materials. MGFs and MGF-based electrodes remain steady conductivities after 100,000 bending cycles at a bending radius of 2 mm. The fb_{FOM} of MGF-based flexible batteries reaches 53.4, around 20 folds higher than industrial products using metal foils.

In Chapter 5, the cathode current collector is modified to operate high-voltage cathode materials by introducing the P element into Ni-coated GFs (NiGFs). Ni/P composite-coated GFs (NiPGFs) have much higher anodic stability: NiPGF shows the onset anodic potential of ~ 4.7 V compared to ~ 4.0 V of NiGF. NiPGF-based electrodes manifest similar rate capability and cyclic stability to Al-based ones, however, the cycle life of the full cell using NiPGF is less than 100 charge/discharge cycles. It is found that the P element shuttles from the cathode to the anode side and influences the solid-electrolyte interface (SEI) components, resulting in a quick capacity decay. The dissolution of P is then restricted by using the atomic layer deposition (ALD) method. Finally, the full cell using protected NiPGF and lithium nickel cobalt manganese (NCM) displays reasonable cycle performance and high flexibility during dynamic bending tests.

In Chapter 6, a lighter and more resilient current collector is developed based on polyethylene terephthalate (PET) fabrics. Compared to the MGFs, the areal densities are further reduced to 2.1 and 2.7 mg cm⁻² for Cu-coated and Ni/P-coated PET fabrics (CuPET and NiPPET). However, PET is not as stable as GFs because of the oxygen-containing groups on the polymer chains. The electroless deposited metal layer features a morphology with some micro-holes which allow the penetration of electrolyte. Fourier transform infrared spectroscopy (FTIR) results illustrate that PET will react with the Li⁺ under the reductive driving force from the electric field at the anode, and finally degrade into aldehydes and alcohol derivatives. It not only leads to inferior coulombic efficiencies (CEs) for CuPET-based anode but also deteriorates the current collector's mechanical performances. To solve this problem, additional electroplating is conducted to fill these micro-holes. The resultant ECuPET shows improved

electrochemical stability, and ECuPET/Gr electrode demonstrates comparable CEs. At last, the full cell using NiPPET and ECuPET presents an energy density of 207 Wh kg^{-1} , 17% higher than the metal foil-based counterpart and 4.5% higher than the MGF-based one. In addition, it displays superior flexibility and durability in two bending test modes: segregated mode and synchronous mode. It maintains a high capacity retention of $\sim 80\%$ after 1500 rigorous bending at radii of 5 mm, 2 mm and 1 mm. Also, in a continuous bending process at the bending radius of 3 mm, the pouch cell work steadily with minor voltage fluctuations, and the discharging capacity is 1.50 mAh cm^{-2} , about 87% of the capacity charging at the flat state.

In summary, a series of fabric-based superlight current collectors are reported in this thesis. GF and PET are two representative materials: the former is an electrochemically inertia material with rigid intrinsic property; the latter is a soft material with lower electrochemical stability in battery systems. With the appropriate protection methods of electroplating and ALD technique, the resultant MGFs and metal-coated PET fabrics (MPETs) are qualified flexible current collectors with comparable electrochemical performances to those metal foils.

7.2 Suggestions for Future Research

Textile-based current collectors are highly promising to be scaled up for future FLBs because of the easy processing, low cost and outstanding comprehensive performance. We have initially demonstrated the feasibility from the fabrication to protection, paving a new way to fabricate high-energy FLBs. To further improve the fabric-based current collectors, it needs to be developed from five aspects:

1. The selection of the substrate materials is important because the final properties of the resultant current collectors are closely related to the intrinsic property of the substrate. As mentioned, GF and PET are two representative materials with different electrochemical stability and mechanical performances. For the former, we should consider how to improve its flexibility through the fabric structure design, while for the latter, preventing side reactions is the most urgent task. Some special requirements on the current collectors can be realized by using specific substrates. For example, if we want to make a high-temperature-resistant current collector, polyimide (PI) is highly recommended to be used as the substrate because of its high melting point.
2. Textile structure is essential for deciding the final mechanical flexibility and durability. Although glass itself is rigid, the GF fabrics show decent flexibility, which is derived from the bending, rotating and sliding of these fibers. In this thesis, the chosen GF and PET fabrics are both plain weaves in consideration of pursuing low areal densities for high energy density. Other weaving technology, such as twill weaving and stain weaving can be applied for specific requirements. In addition, the parameters of the fiber, yarn and fabric will influence the final properties of the textile. Further optimization of the textile structure is believed to endow the current collector with better performance.
3. The selection of coating material and the coating method are vital because they decide the electrical conductivity and electrochemical stability of the fabric-based current collectors. Cu has been proven to be a suitable coating material on the

anode side. The mass loading of $\sim 1 \text{ mg cm}^{-2}$ endows the fabrics with conductivity of $\sim 10^5 \text{ S cm}^{-1}$, an order of magnitude lower than Cu foil. However, no matter the Ni or the Ni/P composite can not provide the fabrics with satisfactory conductivity in a relatively low mass loading. It could be replaced with other more conductive and lighter metals. On the other hand, the ELD process can be optimized for a better quality of coating layer. Another critical factor that needs to be considered is the electrochemical stability. Ni/P composite coating layer can be referred to as a paradigm for high-voltage applications. It should be noticed that Al is still the best choice for the cathode current collector because it is light and cheap, and has excellent electrochemical stability (Protection of Al_2O_3). Exploration on the deposition of Al in the air is very meaningful to the composite current collector for the cathode. Other metals, metal composites or alloys are encouraged to develop for a better comprehensive property. For example, titanium is a charming material for the cathode current collector because it is chemically stable and has the highest strength-to-weight ratio.

4. Protection methods are sometimes required to eliminate the side reactions if the fabricated conductive fabrics are still unstable. Electroplating Cu is a physical protection method to segregate the substrate from the electrolyte. The Al_2O_3 layer prepared by the ALD method can selectively allow the transportation of ions, thus preventing the unwanted shuttling phenomenon. These two methods used in this work can be transplanted to protect other substrates. However, it still needs a universal protection method for the anode and the cathode, by which the selection of the substrate and coating materials can be extended to wider ranges.

5. Commercialization of fabric flexible LIBs is very meaningful to the market of future flexible electronics but it is also full of challenges. At first, the coating of active materials on a large-scale production should be precisely controlled to optimize the final battery performance. Considering that fabrics have much more complex structures than commonly used metal foils, the optimization on the quality of the electrodes will be hard. Another issue is the welding between the metal tab and metal-coated fabrics. The metal coating layers on the fabrics are very thin, always with hundreds of nanometers. Hence, it is hard to obtain perfect welding between the fabric current collector and the metal tab. As a result, high contact resistance in this interface will lead to an inferior battery performance for commercial products. This issue should be addressed before commercialization.

From the selection of the substrate material, textile structure design, coating material and method, protection methods to the commercialization, there are a large number of issues to be solved. It is believed that the lightweight and flexible fabric-based current collector will be applied in commercial FLBs in the near future.

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