Surface and Structure Engineering for Next Generation Lithium Metal Batteries

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SURFACE AND STRUCTURE ENGINEERING FOR NEXT GENERATION LITHIUM METAL BATTERIES

BY

KE CHEN

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This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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Lithium (Li) metal has been considered as one of the most promising anode materials to replace conventional graphite for Li-ion battery due to its high theoretical capacity (3860 mAh g\(^{-1}\)) and low electrochemical potential (-3.04 V vs standard hydrogen electrode). However, it still faces some problems such as unstable solid electrolyte interphase (SEI), uncontrolled Li dendrites growth, and infinite volume change during battery charging/discharging. To develop a stable and low-cost Li metal anode for next-generation Li metal battery, in this dissertation, we have made efforts to understand and solve these problems in two aspects, by introducing an artificial SEI and constructing a 3D porous current collector. Firstly, a multifunctional artificial SEI protective layer was designed via using a nitrogen plasma treatment on the Li metal. A highly [001] oriented Li nitride (Li\(_3\)N) layer was formed on the surface of Li metal with a plasma activation time of fewer than 5 minutes. Due to its high Young’s modulus (48 GPa) and high ionic conductivity (5.02\(\times\)10\(^{-1}\) mS cm\(^{-1}\)), the Li\(_3\)N artificial SEI layer blocked the direct contact between reactive Li metal and the liquid organic electrolyte, and suppressed the Li dendrite formation. Secondly, a highly flexible copper (Cu)-clad carbon framework (CuCF) current collector was designed for Li metal batteries. The pyrolysis of melamine-formaldehyde foam and following Cu electrodeposition were employed to fabricate the CuCF. The advanced current collector exhibited excellent flexibility with uniformly distributed Li nucleation
sites on its surface. The cross-linked fiber network structure with large space could accommodate the volume change, while the high surface area and uniformly distributed Li nucleation sites led to the quench of the formation of Li dendrites.

As a result, a dendrite-free Li metal anode was achieved in both circumstances. The Li$_3$N artificial SEI and CuCF both gave rise to a stable Li plating/stripping with high Coulombic efficiency. In both cases, Li/LCO or Li/LFP full cells exhibited a long cycling life at a high current density of 1C. Furthermore, the Li deposition behavior with an artificial SEI and 3D current collector was also studied and compared with bare Li in the dissertation. The methods and strategies we used in the dissertation can provide a facile approach to realize a stable and safe Li metal anode for next-generation Li metal batteries.
Chapter 1 Introduction: Advances in Li Metal Batteries

1.1 Background

Lithium-ion (Li-ion) batteries have significantly changed our lifestyle, becoming an essential part of our daily life. They have been widely used in many portable devices such as smartphones and laptops. Furthermore, electric vehicles powered by Li-ion batteries have emerged into the market in recent years and become more and more popular around the world. On the other hand, with the increasing concerns of environmental pollutions and fossil fuel shortage, renewable energy has been intensively explored in recent years. According to the Monthly Energy Review published by the U.S. Energy Information Administration[1], 17.5% of the U.S. electricity generation in 2019 is from renewable sources such as hydropower (6.6%), wind (7.3%), and solar (1.8%). To efficiently store the intermittently generated energy, large-scale and reliable energy storage devices are highly demanded. To fulfill the needs of both small portable devices and large scale grid storage, next-generation energy storage devices should have a higher energy density and long cycling life.

Current Li-ion batteries technology using graphite as anode and Lithium nickel cobalt aluminum oxides (NCA) as cathode can deliver an energy density of ~300 Wh kg$^{-1}$, which is more than three times higher comparing to 80 Wh kg$^{-1}$ of the first generation Li-ion battery [2, 3]. However, the development of the Li-ion battery has come to its bottleneck because both anode and cathode have almost reached their theoretical capacity value. Therefore, high capacity and advanced electrode materials are highly needed for
developing next-generation Li-ion batteries. Li metal has been considered as the “holy grail” anode material because of its high capacity of 3860 mAh g\(^{-1}\) and lowest reduction potential of 3.04 V versus standard hydrogen electrode (SHE)[4]. In the Li metal battery, the energy density can reach 500 Wh kg\(^{-1}\) by replacing graphite with Li metal as the anode. Even higher capacity can be further achieved with other emerging cathodes such as sulfur and oxygen. Li metal battery therefore is considered as the next-generation battery technology beyond Li-ion battery.

1.2 Li-ion battery

1.2.1 A brief history of Li-ion battery

After the finding that Li metal has the highest electrode potential of 3.3044 V in reference to a saturated calomel electrode (3.04V vs SHE) by Lewis and Keyes in 1913[5], scientists have started to try to invent a battery based on Li metal or its derivatives. In the 1970s, the Huggins group at Stanford University was studying a group of materials that had layered structures and could host guest-species into these structures. Whittingham, who was from the Huggins research group, was working at Exxon Mobile at that time. He discovered that titanium disulfide (TiS\(_2\)) could serve as an ideal host for Li ions because Li ions could reversibly intercalate/deintercalate into TiS\(_2\) (Figure 1a) [6]. However, TiS\(_2\) is unstable in moist air and easily decomposed. Besides, TiS\(_2\) also has a low potential against Li. Thus, the first generation of Li based battery with TiS\(_2\) as cathode and Li metal anode can only deliver a voltage of ~2.5V. In 1980, Goodenough found that LiCoO\(_2\) could be a suitable cathode material to replace TiS\(_2\), as it had a similar structure to TiS\(_2\) and could revisable store Li ions (Figure 1b). LiCoO\(_2\) also exhibits a much higher potential of 4V against Li [7].
Figure 1.1 (a) Structure of TiS$_2$ with intercalated Li ions. (b) The layered structure of CoO$_2$ with intercalated Li ions.[8]

Although Armand has proposed a battery design that using intercalation compounds as both electrodes at that time, [9]. Li metal was still used as the anode materials because there is no intercalation host was discovered that could act as an anode. In 1988, a company called Moli Energy commercialized the first Li metal rechargeable battery using MoS$_2$ as a cathode which has a similar structure and electrochemical behavior to TiS$_2$ [10]. Fire accidents caused by Li metal dendrites induced short-circuits had Moli Energy recalled these batteries after several months. In 1983, Yoshino found that petroleum coke, an amorphous carbon from the residual petroleum fraction, can be used as the Li ion host and demonstrated the first dual-intercalation battery [11]. Sony finally commercialized the rechargeable battery and named it “Li-ion battery” in 1990. Later graphite was adopted as the anode material with ethylene carbonate-based electrolyte to finalize the well-known graphite/LiCoO$_2$ Li-ion battery structure [12]. To recognize the pioneer scientists, the 2019
Nobel Prize in Chemistry had been awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino for their contribution in developing Li-ion batteries.

1.2.2 Working principle of Li-ion battery

Figure 1.2 shows the working principle of the typical commercial graphite/LiCoO$_2$ Li-ion battery, which compromises a carbon-based anode (e.g. graphite), a metal oxide base cathode (e.g. lithium cobalt oxide), and Li salt contented carbonate-based liquid electrolyte (e.g. lithium hexafluorophosphate (LiPF$_6$) in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC)). Other components such as a polymer separator (e.g. polypropylene (PP)), current collectors (Cu at anode side and Al at cathode side), battery cases are also used. During battery charging, the external power forces Li ions to migrate from the cathode electrode into the layered graphite through the electrolyte. The electric energy is converted to chemical energy and stored in the battery. During discharge, the Li ions go back to LiCoO$_2$ and the electrons travel through the external circuit, powering electronic devices. The chemical reactions happen at cathode and anode are shown in equation (1.1) and (1.2).

$$\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (1.1)$$

$$6\text{C} + x\text{Li}^+ + xe^- \leftrightarrow x\text{LiC}_6 \quad (1.2)$$
1.2.3 Energy density bottleneck of Li-ion battery.

Since the Li-ion battery with graphite anode and LiCoO$_2$ cathode was commercialized in 1991 by Sony, the specific energy has been increased from 80 Wh Kg$^{-1}$ of the 1st generation of Li-ion battery to 300 Wh Kg$^{-1}$, nearly approaching the theoretical value of cathode/anode materials [4, 8]. Meanwhile, the cost has also decreased to 300 US$ kWh$^{-1}$[14]. However, to meet the fast-growing energy demands and develop high-energy batteries for electric vehicles and grid storage applications, the high specific energy of 500 Wh Kg$^{-1}$ and cost below 100 US$ kWh$^{-1}$ at the pack level is needed [2]. One of the strategies to achieve high energy density is to use high-capacity cathode and anode materials. From the cathode side, high nickel content lithium nickel manganese cobalt oxide (NMC) (Ni $> 60\%$) such as NMC622 and NMC811, is one of the choices as NMC holds a higher capacity of more than 200 mAhg$^{-1}$ and high operation voltage (3.8V) [2]. From the anode side, compared to the
graphite anode (specific capacity of 372 mAh/g), Li metal has a high specific capacity of 3860 mAh g\(^{-1}\), as well as a much lower reduction potential (-3.04 V vs SHE)[14, 15]. Besides, the Li Li-sulfur batteries and Li-oxygen batteries had a higher theoretical energy density of 2567 and 3505 Wh kg\(^{-1}\), respectively, in which they both have to use Li metal as their anode.

1.3 Li metal battery

1.3.1 The revisit of Li metal anode

During the development of the Li-ion battery, as discussed above in section 1.2.1, Li was used in Li/TiS\(_2\) battery in every early battery prototype. It was later discarded because of its capacity loss and safety concerns. At that time, graphite was also discovered to serve as a better anode. With the increase of energy density demand, Li metal has become one of the most attractive, if not the only, anode choice for future battery technology to reach the goal of 500 Wh kg\(^{-1}\)(Figure 1.3)[16]. Replacing the graphite electrode with lithium metal, which results in a ~35% increase in specific energy and ~50% increase in energy density at the cell level, provides a path to reach those goals. Therefore, more and more researchers are starting to reconsider Li metal anode in the recent 10 years. In addition, the Li metal anode also opens up a great opportunity for the application in the next-generation energy storage cells including Li sulfur (Li-S) and Li-air batteries. They hold the potential to deliver theoretical energy densities of 2567 Wh kg\(^{-1}\) and 3505 Wh kg\(^{-1}\), respectively.
Different from the insertion-host electrode materials (such as graphite and lithium titanate), Li metal is a conversion-pattern host-less anode. Equation (1.3) describes the reaction that happens at the Li anode side. During charging, Li ions are electrochemically reduced and deposited onto the Li metal surface. During discharge, Li metal is oxidized and dissolved into the electrolyte.

\[ \text{Li} - e^- \leftrightarrow \text{Li}^+ \]  

(1.3)

### 1.3.2 The challenges of Li metal anode

There are several issues while using Li metal as an electrode. Except for the highly reactive feather of the Li metal, the growth of dendrites during the Li deposition is another big issue,
which gives rise to many consequences (Figure 1.4). Firstly, the dendrites could penetrate the separator and cause the inner short circuit of the battery, companying thermal runaway, and even cell explosion. Secondly, side reaction happens because of the increased surface area, which consumes the electrolyte and active Li. Thirdly, “dead Li” will be generated due to the broken of dendrites. The isolated “dead Li” is electrochemically inactive, which causes the capacity loss in the battery. Fourthly, the accumulation of dead Li, depleting of the electrolyte, and the porous structure will increase the cell polarization. Besides, Li anode has an infinite volume change without matrix, comparing to conventional anode materials such as graphite (10%) and silicon (400%). The porous structured Li deposition makes the volume change even larger. All these lead to low Coulombic efficiency (CE) and fast battery failure.[17]

Two theories have been developed to explain the mechanisms behind the dendrite growth until now: space charge theory and non-uniform solid electrolyte interface (SEI) theory.[18] In the first theory, the cations in the vicinity of the negative electrodes will be rapidly consumed with a sharp concentration depletion, which leads to a local space charge with a strong negative electric field [19]. Massive Li ions will electroabsorb and electroplate in a short period, resulting in the formation of dendrites on the Li metal anode surface [3, 20, 21]. To reduce the ions depletion, researchers developed different strategies such as using high concentration electrolyte to increase the ion concentration[22], pulsed charging protocols[23] for replenishing Li+ concentration and using an elevated temperature during battery operation[24]. Another way to reduce the ion depletion is to use a 3D current collector such as carbon[25], copper[26, 27], and nickel foams[28], which could help to reduce the local current density. In the second theory, Li dendrite growth is explained due
to the non-uniform SEI layer and the uneven current collector surface. More Li is deposited at higher ion-conducting sites of the SEI layer on the surface of the Li, which promotes the growth of Li dendrites. In addition, the uneven surface of the current collector affects the electric field distribution and ion flux in the battery because of the electron accumulation at the tips. Li is preferentially deposited to the tips instead of forming a flat layer. Strategies such as adding electrolyte additives [29], and coating a protective layer on Li metal [30] were proved to help obtain a much robust and uniform SEI. However, the requirement for this protective layer is critical, such as high Young’s modulus for blocking the growth of dendrites, high ionic conductivity for transporting Li ions, as well as low electronic conductivity for preventing the top surface deposition.

Figure 1.4 (a) SEM images of Li dendrites. (b) Scheme of Li metal anode failures during battery cycle.[3]

1.4 Recent advances in Li metal protection

1.4.1 Artificial SEI

SEI layer forms when Li anode meets the electrolyte due to the high electronegativity of the Li. It mainly has insoluble inorganic salts (Li₂O, LiF, Li₂CO₃, etc.) and organic products
((CH$_2$OCO$_2$Li)$_2$ and ROLi). However, the species and ratios of each chemical composition might vary in different electrolyte systems depending on the electrolyte compositions[31]. Ideally, the SEI is electrically insulating but Li ion conductive, and it protects the electrode from intercalation by solvent molecules and ions, while protecting these molecules from electrolytic breakdown[32]. The mechanical properties also matters, which could prevent the stress for the volume change from the electrode. The artificial SEI film is defined as a protecting layer on the surface of the Li metal electrode that possesses the functionalities of SEI [33]. The coating layer should be not only chemically stable and dense to prevent Li corrosion by the electrolyte, but also mechanically strong to suppress the growth of dendrites. Besides, high Li-ion conductivity is also desirable [4, 34]. Artificial SEI can be fabricated by depositing a thin film onto the electrode by advanced thin-film techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), spin-coating, and doctor-blading. The deposited artificial SEI usually does not react with Li metal. In another way, chemical species that can react with Li can be selected to be applied to the Li surface. Li compounds form in-situ on the surface of the Li metal surface and act as the artificial SEI. Some representative researches on both approaches have been listed below as examples.

Carbon materials are stable with Li and have been proved to act as artificial SEI. Cui et al.[35] coated a monolayer of interconnected amorphous hollow carbon nanosphere which is chemically stable and mechanically strong to reinforce the SEI. As shown in Figure 1.5a and b, Li could deposit underneath the carbon layer and grow into a column-like shape. The carbon nanosphere layer modified electrode showed a better CE and cycling stability. A very thin layer of MoS$_2$ (10nm) was sputtered onto the Li metal surface by Cha et al.[36,
MoS$_2$ layer can reduce the impedance and interracial contact due to its unique atomically layered structure and its phase-change characteristics (semiconductor to metallic trait) (Figure 1.5c and d). In addition, the MoS$_2$ layer eliminated the preferential sites for the Li dendrite nucleation. An improved cycling performance was seen in both Li-S and Li/NCM811 batteries with MoS$_2$ protection. Similarly, Al$_2$O$_3$ thin layer could be fabricated by atomic layer deposition (ALD) [38, 39] or sputtering [40] method and used as artificial SEI. The Al$_2$O$_3$ layer could mitigate the corrosion from the atmosphere, sulfur, and electrolyte exposure. Al$_2$O$_3$ also can react with Li to form LiAlO$_x$ solid electrolyte, which could enhance the Li-ion transport at the interphase. An ultrathin bilayer of graphite/SiO$_2$ artificial SEI was proposed, in which the graphite act as an electric bridge between Li metal and the electrolyte while the SiO$_2$ improved the electrolyte affinity and Young’s modulus [41]. The multifunctional double-layer artificial SEI improves the cycling stability of the Li/Li symmetric cell to more than 1600 hours at a current density of 0.5 mA cm$^{-2}$. 
Figure 1.5 (a) Schematic showing how interconnected hollow carbon spheres create accommodate the volume change and suppress the dendrite growth. (b) Cross-section SEM image showing columnar Li deposited underneath the carbon nanosphere layer [35]. (c) Schematic showing the fabrication of a thin layer of MoS$_2$ by a sputtering method. (d) SEM images of bare Li and MoS$_2$ coated Li before and after cycling[36].

Polymer materials can also be used as artificial SEI because their flexibility can provide intimate contact with the electrolyte and allow effective suppression of the dendritic Li growth[33]. Guo and co-workers employed Li polyacrylic acid (LiPAA) on Li surface as artificial SEI[42]. A high elasticity was demonstrated by in-situ AFM during Li plating and stripping. The LiPAA film was self-adapted to the volume change of Li plating, and also reduced the side reactions. A stable cycle of 700 hours was demonstrated in LiPAA
protected Li symmetric cells comparing to 300 hours for bare Li. Yu et al. [43] designed a
dynamic single-ion-conductive network (DSN) as a multifunctional artificial SEI with the
features of fast ion transport, conformal protection, and parasitic reaction mitigation. In
their design, tetrahedral Al(OR)4\(^-\) (R = soft fluorinated linker) anions were used as dynamic
crosslinking centers, and soft fluorinated chains (1H,1H,11H,11H-perfluoro-3,6,9-
trioxaoxane-1,11-diol, FTEG) are chosen as inert ligands. All these features enabled a
high-performance Li||NCM full cell.

Due to the high reactivity of Li metal, artificial SEI can be formed in a way that exposing
Li with chosen chemicals, the reaction product act as the artificial SEI. The artificial SEI
layer formed in this method usually has a good attachment to Li metal as it is formed in-
situ on the surface of Li metal. Li metal can be exposed to selected gas such as N\(_2\)[44],
Freon gas[45], and sulfur vapor [46]. LiF has been found to effectively help to regulate Li
deposition, many works have been focused to add fluorinated compounds into the
electrolyte, Lin et al. [45] developed a conformal LiF layer as artificial SEI by exposing
Freon R134a gas with Li metal at a controlled gas pressure and reaction temperature
(Figure 1.6 a and b). LiF coating was also applied onto a 3D layered Li-reduced graphene
oxide electrode. As a result, improved cycling stability and reduced side reactions were
achieved. Li\(_2\)S artificial SEI was demonstrated by Chen et al. [46]. They placed Li above
sulfur vapor at an elevated temperature, Li can react with sulfur to form Li\(_2\)S at the Li metal
surface (Figure 1.6 c). The obtained Li\(_2\)S SEI had a high ionic conductivity, which can
mitigate non-uniform Li flux and dendritic Li deposition (Figure 1.6d). Artificial SEI also
can be obtained by immersing Li into prepared solutions. Li et al. treated Li with
polyphosphoric acid (PPA) dissolved in dimethylsulfoxide (DMSO) to get a Li\(_3\)PO\(_4\)
artificial SEI [47]. The PPA-Li anode exhibits a smooth surface and chemical stability with a high value of Young’s modulus of more than 10 GPa. Pathak et al. [48] used a drop-casting method and applied the SnF$_2$ dispersed electrolyte onto the Li metal surface. A multi-component artificial SEI composed of LiF, Sn, and Li-Sn alloy was formed after the reaction between SnF$_2$ reacted and Li metal. At an optimized thickness, more than 2000 hours of Li plating/stripping cycles were achieved.

**Figure 1.6** (a) Schematic of surface treatment of Li metal with Freon R134a to form LiF coating on the Li metal surface. (b) Cross-sectional SEM image of a LiF-coated Li foil
1.4.2 3D current collectors

According to the Li dendrites growth theory that has been discussed above, Li dendrites tend to grow at a non-uniform Li flux and high current condition. Specifically, Due to the inhomogeneous distribution of charges, Li\(^+\) tends to plate at the defects of the substrate surface that have higher local current density. As reported, the Li-ion concentration is relatively steady at a low current density. However, at higher current density, the cations will be rapidly consumed in the vicinity of the negative electrodes with a sharp concentration depletion \([19, 27]\). This leads to a local space charge with a strong negative electric field, it will electroabsorb and electroplate massive Li ions in a short period, resulting in the formation of dendrites on the Li metal anode surface \([3, 20, 21]\). This behavior for dendrite growth is known as Sand’s behavior as widely reported in the literature \([26, 49, 50]\). The Sand’s time equation (Equation 1.4) describes that the initiation time of dendrite growth (\(\tau\)) is significantly affected by the applied current density \(J\), where \(J\) is effective electrode current density, \(D\) is the ambipolar diffusion coefficient, \(e\) is the electronic charge, \(C_0\) is initial Li salt concentration, and \(t_a\) is anionic transference number.\([51]\) Compare to the planar current collector, the 3D current collector has a much higher surface area, which reduces the local current density of the Li metal anode, thus mitigate the dendrite growth. Similarly, the Li dendrite growth rate (\(V_{\text{tip}}\)) is also found to be reduced at a lower current density \(J\) (Equation 2), where \(V\) is molar volume and \(F\) is
Faraday’s constant.[52] Besides, submicron ranged structures in the 3D current collector induce a homogenous charge distribution, eventually leading to a relatively even Li deposition.[53] In addition to the reduced local current density, the 3D current collector also functions as a Li host which could reduce the volume change[4]. With all Li depositing into the skeleton of the 3D structure, a stable SEI may form without broken due to the volume change [54].

$$\tau = \pi D \left( \frac{e C_0}{2 j t_a} \right)^2 \quad (1.4)$$

$$V_{\text{tip}} = \frac{IV}{F} \quad (1.5)$$

Guo et al. [53] fabricated a 3D Cu current collector with a submicron-sized skeleton and porous structure and further studied the Li deposition behavior on a 3D current collector. They found Li can be accommodated into the pores with suppressed dendritic Li. Figure 1.7 a and b shows Li deposition differences between planar Cu and the 3D current collector. At the first deposition step, Li tended to form small nuclei which function as a charge center due to the charge accumulation at the sharp end in the electrical field. The subsequent Li was then deposited on the nuclei and promoted the continuous growth of dendrites (Figure 1.7a). In 3D Cu current collector with a submicron skeleton, the numerous fibers worked as the charge center and led to a uniform electrical field and homogenous charge distribution (Figure 1.7b). Therefore, Li was expected to nucleate on the Cu fibers and fill the pores of the 3D current collector. As a result, a smooth Li surface could be obtained. Similarly, Ni foam 3D current collectors were proposed. A Li-Ni composite electrode was prepared by immersing Ni foam into a melted Li, [28]. Ni foam not only could host Li into
its 3D structure but also accommodated the surface energy between Li metal and electrolyte during cycling (Figure 1.7c). To improve the lithiophilicity of the 3D metal current collectors, N-doped graphene was coated on to the 3D current collector[55]. Figure c and d showed the differences of the current collector with and without N-doped graphene coating. Due to the irregular surface of the non-coated 3DCu, Li dendrites grew on the surface irreversibly. The SEI also tended to broke after Li was stripped. The N-doped graphene contributed a uniform Li flux with scattered distribution of electrons, therefore, leading to a stable SEI and uniform Li deposition (Figure 1.7d). Other lithiophilic coating could also work in a similar way such as Au[56], Ag[57], Sb[58], and ZnO[59]. A multiple layered structure with electrical conductivity and lithiophilicity gradient structure have been developed, which has an Al$_2$O$_3$ coating on top and Au coating at the bottom of a Ni foam (Figure 1.7e)[60]. In this structure, a regulated bottom Li deposition was observed due to electrically passivation of the top Al$_2$O$_3$ coating and lithiophilic bottom Au coating (Figure 1.7 f and g).
Figure 1.7 Schematic of electrical field distribution on (a) planar Cu and (b) 3D current collector [53]. Schematic of Li deposition on (c) 3D Cu current collector and (d) N-doped graphene-coated 3D Cu current collector [55]. (e) Structure of 3D current collector with conductivity and lithiophilicity gradient. (f) Illustration and (g) SEM images of Li bottom-deposition [60].
Other than metal-based 3D current collectors, materials such as carbon-based materials or polymers can also work as the current collector. In comparison, carbon and polymer-based current collector are usually more flexible with a much lower density than metal-based current collectors, which enables a high energy density and flexible energy storage devices. Numerous carbon materials have been explored such as graphene, carbon nanotubes, and electrospun carbon nanofibers. Zhang et al. [61] found that N-containing groups (pyridinic and pyrrolic nitrogen) in the N-doped graphene is lithiophilic with high binding energy to Li, which could introduce a uniform Li nucleation (Figure 1.8a). They used N-doped graphene as the Li plating matrix/current collector and achieved a high CE of 98% after 200 cycles (Figure 1.8b and c). An electrospun mesoporous carbon film with –NH functional group was used as a lithiophilic Li host[62]. As shown in Figure 1.8d, Li could be easily infused into the pores and coated on the surface of the carbon fibers after –NH functional group modification. The Li-C surface was gradually self-smoothed on the 3D architecture during the Li plating/stripping cycles. Figure 1.8e showed the SEM image of the C-Li composite electrode after 200 battery cycles, it became completed smooth without any dendrite. In a practical condition with a high cathode loading, low N/P ratio, and lean electrolyte, the Li-C composite electrode achieved high energy densities of 353 Wh kg\(^{-1}\) and 381 Wh kg\(^{-1}\) coupled with NCM622 and NCM811 electrode, respectively, at a single-cell level. Most of the conductive 3D current collectors might have a problem of “surface deposition” because Li tends to be deposited at where Li ions meet electrons. The surface growth can lead to the volume change and undesirable growth of Li dendrites (Figure 1.8f).
Liu et al. [63] infused melt Li into a polymeric matrix as Li metal anode. Due to the non-conductive nature of the matrix, Li plating and stripping could be well confined.

**Figure 1.8** (a) Binding energy of a Li atom with Cu, graphene, and other N-contain functional groups. (b) Surface morphology of N-doped graphene after 0.5 mAh cm-2 Li was deposited. (c) CE test of planar Cu and N-doped graphene [61]. (d) Schematic figures of self-smooth Li-C nanofiber composite Li anode. (e) SEM images of Li-C
anode after 200 cycles. (f) Schematic of Li plating and stripping process in conductive and non-conductive 3D current collectors.

1.5 Motivation and objectives

1.5.1 Motivation

To reach the 500 Wh kg\(^{-1}\) goal of the next-generation battery, a safe and stable Li metal anode is urgently needed. However, uncontrollable Li dendrite growth and unstable SEI formation hinder the commercialization of Li metal anode. Therefore, a facile and universal strategy to obtain a dendrite-free Li metal anode is highly demanded.

1.5.2 Objectives and outline

The objective of this dissertation is to achieve a dendrite-free Li metal anode with a long cycling life and high CE. Two approaches will be studied in this research by using artificial SEI and 3D current collectors to suppress the dendrite growth and accommodate the volume change. Highly ionic conductive materials Li\(_3\)N and Cu-clad carbon framework are used to demonstrate the effects of artificial SEI and 3D current collector on the Li deposition, respectively. The electrochemical performance of the Li metal batteries and Li deposition behaviors are studied and discussed.

In Chapter 2, a new method to obtain a highly ionic conductive Li\(_3\)N protective layer by plasma treatment on the Li metal surface is introduced. Li\(_3\)N fabrication conditions are first studied and optimized. The effects of plasma treatment time on the Li\(_3\)N crystal structure and morphology are then discussed. Symmetric cell cycling tests are used to examine the Li plating and stripping performance of the Li\(_3\)N artificial SEI protected Li metal anode. The results are compared with the bare Li and Li\(_3\)N layer fabricated in the traditional
method. The contributions from the optimized Li$_3$N thickness, high oriented crystal structure, and superior ionic conductivity are further discussed to correlate the outstanding performance. Postmortem analysis is conducted to check the surface morphology after Li was deposited on the electrode.

Chapter 3 introduced a 3D flexible current collector which is fabricated by a simple two-step method of carbonization and Cu electroplating. The Li nucleation site distribution and conductivity of the current collector are tuned by changing the Cu loading. Li deposition morphology on different kinds of current collectors is compared to study the effects of the current collector on the Li dendrite growth. With the help of the reduced current density and uniformly distributed Li nucleation sites, Li can be confined into the framework without dendrite formation. The CE, symmetric cell cycling, and full cell cycling are tested under different current densities. Besides, the flexibility of the 3D current collector is also investigated, which shows that CuCF has the potential for future flexible/wearable electronics.

Chapter 4 summarizes the findings and significance of this dissertation. Future works are proposed that may make the project more advanced. Strategies to fabricate practical Li metal batteries with artificial SEI and 3D current collectors are also proposed.
Chapter 2 Plasma enhanced formation of Li₃N as artificial SEI for Li metal batteries

2.1 Introduction

Lithium (Li) metal has been considered as the “holy grail” for Li-ion batteries thanks to its high theoretical specific capacity (3860 mAh g⁻¹) and low reduction potential (-3.04 V versus standard hydrogen electrode) [3, 4]. By replacing the conventional intercalation-based graphite anode (specific capacity of 372 mAh g⁻¹) with Li metal in Li-ion batteries, the specific energy and energy density can be improved by more than 35% and 50%, respectively [14, 15]. Moreover, the high capacity of Li metal anode opens up a great opportunity for the application in the next-generation energy storage cells including Li sulfur (Li-S) and Li-air batteries. They hold the potential to deliver theoretical energy densities of 2567 Wh kg⁻¹ and 3505 Wh kg⁻¹ respectively, which are much higher than the performance in the present commercial battery technology [64, 65]. However, the SEI layer formed spontaneously on the Li metal surface is very unstable and fragile. The break and reform of the SEI layer during the plating/stripping process can consume Li and electrolyte

*Chapter 2, in full, is a reprint of the paper “Flower-shaped lithium nitride as a protective layer via facile plasma activation for stable lithium metal anodes” as it appears in the Energy Storage Materials, Ke Chen, Rajesh Pathak, Ashim Gurung, Ezaldeen A. Adhamash, Behzad Bahrami, Qingquan He, Hui Qiao, Alevtina L. Smirnova, James J. Wu, Qiquan Qiao*, Yue Zhou*, 2019, 18, 389-396. Ke Chen was the primary investigator and first author of this paper.
quickly[66], leading to a low coulombic efficiency and severe capacity decay. Furthermore, Li tends to form needle-like dendrites that can penetrate the separator eventually and cause safety issues such as the short circuit of the battery[67, 68]. One of the most effective strategies to address these issues is to introduce suitable protective layers between the Li metal electrode and the electrolyte. Those layers will provide an artificial protective shell to stabilize the SEI and suppress the growth of lithium dendrites. Considerable efforts have been made to select superior materials which can be mainly divided into two categories: inorganic materials such as Li$_3$PO$_4$[47], carbon materials[35, 69] and Al$_2$O$_3$[70]; and organic materials such as polyethylene oxide (PEO) [71] and Nafion[72]. Although those materials can suppress lithium dendrite growth to some extent, they still suffered from some drawbacks including complicated preparation process, low mechanical strength, and/or low Li ion conductivity[3].

It is noted that solid-state lithium ionic conductors are good candidates that can offer high ionic conductivity and have recently been employed as interfacial layers with the mechanical strength comparable to ceramic materials [73, 74]. Among those, lithium nitride (Li$_3$N) has been demonstrated to be a promising solid-state ionic conductor due to the high room temperature ionic conductivity of 6×10$^{-3}$ S cm$^{-1}$ and high Young’s modulus [75-77]. Notably, Li$_3$N can be prepared easily on the top of Li metal by placing Li metal under the nitrogen atmosphere according to the reaction 6Li (s) + N$_2$ (g) → 2Li$_3$N (s). Wu et al. fabricated a Li$_3$N film with $\alpha$- and $\alpha'$-Li$_3$N combined phases by exposing Li metal to N$_2$ in a sealed container [44]. They demonstrated that Li metal protected by Li$_3$N also could be used in Li-S battery to suppress the shuttle effect [78]. Zhang et al. further investigated the Li$_3$N formation condition by controlling the gas flow rate and reaction temperature.
They found that Li$_3$N formed at room temperature with a N$_2$ flow rate larger than 100 sccm for 2 hours showed the best electrochemical performance among other conditions and bare Li [79]. However, the Li$_3$N layer grown at room temperature had a porous structure that can still allow the electrolyte to pass through, thus making the system susceptible to the growth of Li dendrites at long cycles. Cui et al. hence prepared a pin-hole-free Li$_3$N from molten Li and demonstrated its potential application as a solid electrolyte [80]. Despite some successes, all those fabrication methods have the same issue of long growth time (several hours) due to limiting N$_2$ diffusion, which makes this process very time consuming and high cost [81, 82]. Meanwhile, the uncontrolled fabrication process leads to mixed crystal orientations including [100], [001], and [110] [44], which cannot rectify the uniform transport of Li ions and suppress Li dendrite growth efficiently. Therefore, developing a facile and controllable method in a short time and low cost toward the Li$_3$N protective layer with pure crystal orientation is still challenging.

Here in this work, we employ a novel efficient and scalable plasma technique to achieve a desired Li$_3$N film on the Li metal electrode as the protective layer by plasma activation under N$_2$ environment in a very short time (within minutes). The obtained Li$_3$N layer showed a unique flower shape with pure [001] plane orientation, leading to a high Young's modulus and high ionic conductivity. Hence, by introducing this stable protective Li$_3$N layer, the cycling life in a symmetric cell can be enhanced dramatically. A Li-LiCoO$_2$ full cell based on the Li$_3$N protected Li anode also demonstrates a lower overpotential and stable cycling with a high capacity retention of more than 96% after 100 cycles and superior rate capability compared to bare Li anode.
2.2 Experimental

2.2.1 Plasma activation experiment setup

As shown in Figure 2.1, the lab-made plasma setup consists of a quartz tube with two electrode contacts, a vacuum pump, a radio frequency (RF) power supply, and a gas flow meter connected to the gas tank. During operation, a vacuum atmosphere was first established and then RF power was applied to the metal contact. After certain gas was passed through the quartz tube, the gas molecules were ionized and created a plasma atmosphere inside the chamber.

**Figure 2.1** (a) Schematic figures of plasma setup and (b) photos of nitrogen plasma discharge glow.
2.2.2 Preparation of in-situ grown Li$_3$N layer

Li metal chips (MTI corp. thickness is 450 µm) surface were scratched by a sharp blade in the Ar-filled glovebox (moisture and oxygen level <0.1 ppm) to remove the surface oxidation layer and other contaminants before use. A tightly sealed vessel was then used to transfer Li chips from the Ar-glove box into a lab-made plasma chamber. Nitrogen gas was passed through at a flow rate of 200 sccm after a vacuum was created in the tube. The power was set to 125W with a radio frequency of 13560 kHz to create nitrogen plasma. Different treatment times ranged from 1 minute to 4 minutes was used. After plasma treatment, the Li chips were then quickly transferred back into Ar-glovebox for further characterization and battery assembling.

The samples obtained at different plasma treatment times have been defined as LN-1, LN-2, LN-3, and LN-4, respectively. To compare the difference between plasma-treated samples and the samples without plasma, a control experiment was conducted according to previous work [78, 79]. Li chips were put into the plasma chamber with the same N$_2$ flow rate of 200 sccm, to get a thicker Li$_3$N layer, the Li chips were put under N$_2$ flow for 2 hours without applying plasma power. The control sample was labeled as LN-C.

2.2.3 Characterization

2.2.3.1 Scanning electron microscope (SEM)

Hitachi S-3400N scanning electron microscope was used to exam the morphology of the samples before and after battery cycling. The cross-sectional sample was prepared by cutting the samples with a sharp blade in the glovebox. A sealed container was used while transferring the sample from the glovebox to the SEM chamber. SEM images at different
magnifications were taken at an acceleration voltage of 5KV with a sample examination distance of ~10 mm.

2.2.3.2 X-ray diffraction (XRD)

XRD was conducted using a Rigaku SmartLab diffractometer with a Cu target (\(\lambda=1.5406\text{Å}\)) at the 30KV and 20 mA. The 2θ Scanning angles were set from 10 to 70° with the scanning speed of 4° min\(^{-1}\). All the samples were encapsulated with Kapton tape during XRD measurement to avoid moisture contamination.

2.2.3.3 Young’s modulus measurement

Quantitative nano-mechanical (QNM) mode was used for Young’s modulus measurement by Bruker atomic force microscopy (AFM).

2.2.3.4 Contact angle measurement

The electrolyte contact angle of bare Li and plasma-treated samples was measured by the VCA2000 video contact angle system to test the wetting property.

2.2.4 Electrochemical measurements

CR2032 coin cell structure was used for all the battery assembly and tests. Celgard 2325 film of 25 µm thickness was used as the separator and 1M LiFP\(_6\) in the mixture of ethylene carbonate (EC) / dimethyl carbonate (DEC) (1:1 v/v) (Sigma Aldrich) as the electrolyte. All the cells were assembled in the Ar glovebox.

2.2.4.1 Symmetric cell test

For symmetric cells, the same samples were used at both electrodes of the cell. The as assembled cells were discharged by a Land battery analyzer (LANHE CT2001A) at a
current density of 0.5 mA cm\(^{-2}\) with a total capacity of 1mAh cm\(^{-2}\) and then charged at the same current and capacity. A larger current of 1 mA cm\(^{-2}\) with a higher capacity of 2 mAh cm\(^{-2}\) was also tested.

2.2.4.2 Full cell test

Lithium cobalt oxide (LCO) was used as cathode materials. LCO electrode was prepared by mixing LCO (MTI corp.), Super P carbon and polyvinylidene fluoride (PVDF) at a weight ratio of 8:1:1 in N-Methyl-2-pyrrolidone (NMP) solvent. After overnight stirring, the obtained slurry was cast onto aluminum foil by a doctor-blading method and then dried in a vacuum oven for 12 hours. The active material mass loading was about 4 mg cm\(^{-2}\). Li/LCO full cells were charged to 4.2V and then discharged to 3 V at 0.2C (1C=140 mAh g\(^{-1}\)) for the first cycle and 1C for the following cycles. Full cells were also tested at the different current of 0.5C, 1C, 2C, and 5C to test their rate performance.

2.2.4.3 Electrochemical impedance spectroscopy (EIS)

VersaSTAT3 (Princeton Applied Research) was used for the EIS test. The frequency range was set from 0.1Hz to 100K Hz for both symmetric cells and full cells.

2.3 Results and discussion

2.3.1 Crystal structure analysis

XRD was used to study the phase changes after nitrogen plasma activation. In order to protect the reactive sample from contamination of air and moisture, Kapton tape was used to cover the samples. As shown in Figure 2.2a, the Kapton tape only has a wide diffraction peak at around 20\(^{\circ}\), which can easily be distinguished from Li and Li\(_3\)N peaks. Pure Li
metal shows peaks at 36°, 52°, and 65°, which are corresponding to (110), (200), and (211) planes (PDF #15-0401) [78, 79]. After N₂ plasma activation, α-phase Li₃N was formed (PDF #30-0759) in a short time. With activation time increases from one minute to three minutes, the Li₃N peaks intensity becomes higher which indicates a higher crystallization. In addition, the distinct (001) and (002) diffraction peaks reveal that Li₃N film obtained by N₂ plasma activation is highly oriented along the direction vertical to the Li surface [80, 83]. In comparison, LN-C obtained under N₂ flow without plasma shows a polycrystalline structure with (001), (100), (002), (110), and (102) peaks (Figure 2.2b), which is similar to the Li₃N film grown in room temperature previous reported [44, 78, 79]. The Li peaks still can be found in the XRD patterns in both plasma-treated samples and the control sample because Li₃N formed on the surface of Li metal is very thin. Figure 2.3 shows a crystal structure of α-phase Li₃N. It is a layered structure with hexagonal Li₂N layers connected by the Li ions layer. This special N-Li-N structure provides open tunnels for Li ion transfer which offers an excellent Li ion conductivity and lower Li⁺ ions migration energy barriers [75, 76, 84]. Comparing to a multi-crystalline structure, it has fewer defects and could provide more mechanical strength to suppress the dendrite penetration. It is worth noted that no contaminates (such as LiOH, Li₂O, or Li₂CO₃) are introduced to the electrodes in both conditions either by plasma activation or the traditional gas flow process according to the XRD patterns, which ensures that all the battery performance improvement are coming from the artificial SEI layer in the following discussion.
Figure 2.2 (a) XRD patterns of Li$_3$N films at different plasma activation time. (b) XRD patterns of Li$_3$N prepared without plasma.

Figure 2.3 Li$_3$N crystal structure which compromises a layer of Li$_2$N and a layer of Li.
2.3.2 Morphology of Li\textsubscript{3}N

The color of pure Li is shining silver as shown in Figure 2.4a inset. Due to the formation of Li\textsubscript{3}N, the color changes into dark black (Figure 2.4d, g, and j inset). SEM images of bare Li shows a relatively smooth surface at a lower magnification (Figure 2.4a). However, defects still can be noticed at high magnification (Figure 2.4b). These defects can serve as nuclei, which lead to an uneven Li deposition and the formation of dendrites during the Li plating process [85]. On 1-minute plasma-activated sample (LN-1), flower-shaped Li\textsubscript{3}N clusters are formed on the surface of Li metal as shown in Figures 2.3d, e, and f. The Li\textsubscript{3}N is not covered on the whole surface of the Li metal. The clear color contrast between Li\textsubscript{3}N clusters and background Li metal under SEM can be noticed from Figure 2.4d and e, in which Li\textsubscript{3}N is much brighter than Li metal. The reason can be attributed to the accumulation of charges on the electronically insulated Li\textsubscript{3}N under the SEM electron beam [44]. As shown in Figure 2.4g-i and j-l, a denser Li\textsubscript{3}N layer is formed on top of the Li metal surface at 2-minute and 3-minute treatment respectively. Zhang et al. had proposed an island-growth mechanism for Li\textsubscript{3}N [79] that Li\textsubscript{3}N first grows at the defect spots to form a nucleus and then extends into two dimensions overwhelmingly and forms a dense Li\textsubscript{3}N layer. This island-growth mechanism can perfectly fit into the Li\textsubscript{3}N formation here. The thickness of the Li\textsubscript{3}N layer can be measured from the cross-sectional SEM images (Figure 2.3f, i, and l). In LN-1, the Li\textsubscript{3}N layer is an incomplete film. With the plasma activation time increase, the thickness is increased to \(\sim8\mu\text{m}\) at 2 minutes and then \(\sim30\mu\text{m}\) at 3 minutes. It should be mentioned that the thickness of the Li\textsubscript{3}N layer based on plasma activation technology can be controlled accurately by simply adjusting treatment time (only several minutes) with wide thickness range.
In order to prove that the layer of Li$_3$N can be grown much thicker, a sample at a higher treatment time of 4 minutes was also prepared. As shown in Figure 2.5a and b, LN-4 exhibits a much larger gain sized than the samples obtained at lower treatment time. The thickness of Li$_3$N is also increased significantly to ~100 µm (Figure 1.5c). As reported in previous work [44, 78, 79], due to the diffusion limit, the growth rate of Li$_3$N is only several hundreds of nanometers per hour (~20 nm/min) when putting Li under N$_2$ atmosphere without plasma treatment. However, a hundred times higher Li$_3$N growth rate is found in this study (>10 µm/min) (Figure 2.5d). It is because nitrogen gas molecules, ions, and atoms are highly energetic in a plasma condition. In addition, the heat generated from plasma also accelerates the reaction, which makes the reaction 3Li + N$^+$ → Li$_3$N more efficient.
Figure 2.4 SEM images of bare Li and Li$_3$N film obtained at different N$_2$ plasma times. (a-c) Digital (a inset) photo, surface (a and b) and cross-section(c) of bare Li. (d-f) Digital photo (d inset), surface (d and e), and cross-section (f) of Li$_3$N film after 1-minute N$_2$ plasma activation. g-i) Digital photo (g inset), surface (g and h), and cross-section (i) of Li$_3$N film after 2-minute N$_2$ plasma activation. (j-l) Digital photo (j inset), surface (j and k), and cross-section (l) of Li$_3$N film after 3-minute N$_2$ plasma activation.
2.3.3 Young’s modulus analysis

Young’s modulus was measured by atomic force microscopy (AFM) and an average value was then extracted from the mapping at area 10 by 10 µm range. Figure 2.6a, c, and e show the topography of bare Li, Li$_3$N obtained under N$_2$ flow, and Li$_3$N obtained under N$_2$ plasma, respectively. The surface of bare Li is relatively flat with a surface roughness at the range of less than 0.2 µm. With the formation of Li$_3$N, the roughness is significantly increased to 0.8 µm for LN-C and 1.7 µm for LN-2. This is because of the flower-shaped
Li$_3$N formation after nitrogen plasma and is correlated to the SEM images in Figure 2.4. The corresponding Young’s modulus mappings are displayed in Figure 2.6b, d, and f. The average value is of bare Li is calculated to be 0.65 GPa. After 2 minutes of plasma treatment with the Li$_3$N layer on top, LN-2 shows a high Young’s modulus of 48 GPa, which is more than enough to suppress the formation of Li dendrites. Theoretically, Li dendrites can be mechanically blocked if the modulus of a protective layer is larger than 6 GPa [86], therefore, Li$_3$N layer could easily block the growth of Li dendrites. The high modulus of LN-2 can be attributed to its highly orientated crystal structure, which induces a compact and dense film on top of Li metal. In comparison, Young’s modulus of LN-C was also measured, the value is only 4 GPa, which is lower than the required modulus of 6 GPa. As expected, LN-C could help to improve the performance of Li metal anode to a certain extent but still inferior to plasma-treated samples.
Figure 2.6 Topography and corresponding Young’s modulus mapping of bare Li (a and b), LN-C (c and d), and plasma-treated Li$_3$N layer (e and f).

2.3.4 Symmetric cell test

The Li plating and stripping stability of bare Li and plasma-treated Li metal anodes were investigated by symmetric cell cycling tests. In this test, during each cycle, 1 mAhr cm$^{-2}$ of Li was firstly plated onto the working electrode (bare Li or plasma-treated Li) at a current
density of 0.5 mA cm\(^{-2}\) and then 1 mAh cm\(^{-2}\) of Li was stripped. The voltage profiles during the plating/stripping cycles are recorded. As shown in Figure 2.7a, the overpotential of bare Li symmetric cell increases considerably after only 75 cycles, indicating an increase of cell resistance and voltage built-up. There are two main reasons attributes to the early failure of the bare Li cell. Firstly, the continuous formation of SEI consumes electrolytes. SEI is formed naturally on Li metal when contacting with the electrolyte. However, the SEI is very fragile and unstable which breaks easily because of large volume change during Li deposition. Fresh Li under the SEI is then exposed to the electrolyte and resulting in further consumption of electrolyte to form new SEI. The electrolyte is therefore dries up quickly in bare Li cell. Another reason is the formation of “dead” Li. Li dendrites form on the surface of the Li electrode due to the uneven deposition. During Li stripping, Li dendrites broke down and therefore isolate from the base Li metal, which causes the formation of inactive “dead” Li accumulating on top of the electrode. The thick layer of “dead” Li could largely increase mass transfer resistance[87]. Thanks to the dense Li\(_3\)N layer protection, much longer cycling life was shown in N\(_2\) plasma-treated samples. The 2-minute plasma-activated sample (LN-2, Figure 2.7c) shows the best performance with a stable voltage profile even after 30,000 minutes (500 hours). In LN-2 cells, direct contact between Li metal and the electrolyte is blocked, which prevents the continuous formation of the SEI layer. Also, the small tips of Li\(_3\)N grains lead to a more uniform Li flux due to the uniform electronic field distribution, which eliminates the Li deposition hot spots [53, 88]. With an optimized thickness of 8 \(\mu\)m in LN-2 cells, Li ions can pass through easily and deposit underneath the ionic conductive Li\(_3\)N layer. Li dendrites are thus physically suppressed by the Li\(_3\)N layer. As shown in Figure 2.7b and d, a not fully covered Li\(_3\)N layer obtained at
1 minute (LN-1) or too thick layer (LN-3) have inferior cycling performance than LN-2 but still better cycling life than bare Li. In LN-1, the formation of the Li₃N cluster increases the electrolyte wettability of the electrode, which can prevent Li dendrites growth and hence delay the process of cell failure [89, 90]. For LN-3, the thicker Li₃N layer (~30 µm) hinders the Li migration between Li metal and electrolyte, leading to cell failure earlier than the LN-2.

Figure 2.7 The symmetric cell cycling test of (a) bare Li, (b) LN-1, (c) LN-2, and (d) LN-3.
The voltage profiles at the beginning, after 100th, and 200th cycles are magnified and shown in Figure 2.8. At the beginning of the test, all three samples are exhibiting identical voltage profiles (Figure 2.8a). The bare Li shows the lowest stripping overpotential in a magnified position (Figure 2.8b). With the increased thickness of the Li$_3$N layer, the overpotential is slightly increased. It is because Li ion transfer channels have not been initiated yet at the beginning of the cycles. LN-2 exhibits a flat voltage profile with a lower than LN-1, LN-3, and bare Li cells after 100 cycles as shown in Figure 2.8c. The overpotential of LN-2 is further reduced after 200 cycles (Figure 2.8d) indicating a stable plating/stripping of Li and the establishment of a high Li ion conductive channel between Li metal and electrolyte. A stable interface is also formed between Li metal and liquid electrolyte. These phenomena are going to be further discussed later in the next section.
Figure 2.8 (a) Voltage profile of the beginning cycles. (b) The zoomed-in figure of the first stripping cycle. Voltage profile at the (c) 100th cycle and (d) the 200th cycle.

To ensure that Li$_3$N protected sample works at an elevated current density and capacity, a current density of 1 mA cm$^{-2}$ with a total capacity of 2 mAh cm$^{-2}$ was applied to LN-2 and bare Li in symmetric cell test. Due to the high ionic conductive and high Young’s modulus Li$_3$N layer, the LN-2 sample can keep a stable Li deposition/stripping for 12,000 minutes (Figure 2.9). In comparison, bare Li symmetric cells could only last less than 8,000 minutes at the same current density.
2.3.5 Ionic conductivity

The kinetics of the Li$_3$N protection layer are studied by EIS measurement which provides the information of charge transfer resistance at the Li metal/electrolyte interface. EIS of symmetric cells was measured before battery cycling and after 50 charge/discharge cycles. As shown in Figure 2.10, there are two semi-circles in the spectra. The first semi-circle at the higher frequency can be assigned to Li ions diffusion resistance in the Li$_3$N film or SEI, while the second semi-circle is attributed to charge transfer resistance at the Li metal/electrolyte interphase [91, 92]. The data were fitted using an equivalent circuit shown in Figure 2.10b inset and fitting results are listed in Table 2.1. Before cycling, the plasma-treated samples exhibit a little higher charge transfer resistance than bare Li because Li$_3$N layer hinders the charge transference before cycling and an activation process is needed. However, a large reduction of charge transfer resistance is found after 50 cycles since Li$_3$N.
forms a stable interface with high Li ionic conductivity pathways (Figure 2.10b). These EIS results are consistent with the flat Li plating/stripping curves in Figure 2.8.

Li ion conductivity of Li$_3$N can be calculated based on EIS data[80]. In bare Li, the series resistance $R_s$ equals the overall resistance (3.5 Ω) from the electrolyte and contact. In LN-2 or LN-3 symmetric cells, the $R_s$ consist of electrolyte resistance, contact resistance, and Li$_3$N layer resistance as well. Therefore, the Li$_3$N layer resistance of LN-2 can be easily obtained by $R_s$(LN-2) – $R_s$(bare Li). The ionic conductivity of Li$_3$N then can be calculated using the equation $\sigma = 2 L/Ra$, in which, $L$ is the thickness of Li$_3$N, $R$ is the resistance of Li$_3$N and $a$ is the area. The ionic conductivity of Li$_3$N is calculated as $5.03 \times 10^{-1}$ mS cm$^{-1}$ for LN-2 before the cycle. The superb ionic conductivity can be attributed to the unblocked Li ion transport channels along [001] direction in Li$_3$N grains. Anionic conductivity larger than $5\times 10^{-1}$ mS cm$^{-1}$ is typically required for battery operation in an artificial SEI layer or solid-state electrolyte [93]. Therefore, the ionic conductivity of the plasma-activated Li$_3$N layer is high enough to establish a fast Li ions exchange channel between Li metal and liquid electrolyte.
Figure 2.10 Electrochemical impedance spectra of bare Li and plasma-treated samples.

(a) EIS of symmetric lithium cells of bare Li, LN-1, LN-2, and LN-3 (a) before cycling and (b) after 50 cycles. (b inset) The equivalent circuit for EIS fitting.

Table 2.1 EIS fitting results of bare Li, LN-1, LN-2, and LN-3 symmetric cells before cycling and after 50 cycles.

<table>
<thead>
<tr>
<th></th>
<th>Rs before cycling (Ω)</th>
<th>Rs after 50 cycles (Ω)</th>
<th>RSEI before cycling (Ω)</th>
<th>RSEI after 50 cycles (Ω)</th>
<th>Rct Before cycling (Ω)</th>
<th>Rct After 50 cycles (Ω)</th>
</tr>
</thead>
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<tr>
<td>Bare Li</td>
<td>3.5</td>
<td>5.2</td>
<td>223.2</td>
<td>225</td>
<td>108.0</td>
<td>51.1</td>
</tr>
<tr>
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<td>5.2</td>
<td>3.8</td>
<td>277.2</td>
<td>201.6</td>
<td>191.3</td>
<td>37.6</td>
</tr>
<tr>
<td>Material</td>
<td>Modulus</td>
<td>Ionic Conductivity</td>
<td>Young’s Modulus</td>
<td>Ionic Conductivity</td>
<td></td>
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<tr>
<td>LN-2</td>
<td>5.9</td>
<td>13.2</td>
<td>307.0</td>
<td>98.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LN-3</td>
<td>13.2</td>
<td>17.2</td>
<td>352.6</td>
<td>128.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LN-C</td>
<td>5.1</td>
<td>4.9</td>
<td>412.0</td>
<td>223.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.11 shows the modulus and ionic conductivity data of plasma-activated Li$_3$N together with those of other related work on the artificial SEI layer in Li metal batteries [40, 94-97]. It is noted that this work shows the highest Young’s modulus and fairly high ionic conductivity among the similar approaches. The high Young’s modulus and ionic conductivity can be attributed to the high orientation of obtained Li$_3$N which provides both superior mechanical and electrical properties.

**Figure 2.11** The comparison of Young’s modulus and ionic conductivity value of plasma-activated Li$_3$N with those of other literature reported artificial SEI.
2.3.6 Comparison with Li$_3$N prepared by the traditional method

The control sample (LN-C) was prepared based on previous works by exposing the Li chips under continuous N$_2$ flow for two hours without applying plasma and other parameters are kept the same. The LN-C sample shows a porous morphology with multiple cracks like features (Figure 2.12 a and b). The electrolyte can easily reach Li metal through the cracks and have side reactions. Due to the low Young’s modulus of only 4 Gpa, Li dendrites can easily form and penetrate this layer. LN-C after cycling was examined by SEM and shown in Figure 2.12c. As expected, LN-C has a rough surface with big particles “dead Li”. Similarly, the ionic conductivity was calculated using the same method discussed above. The ionic conductivity for LN-C is $9.4 \times 10^{-2}$ mS cm$^{-1}$ which is much lower than the Li$_3$N with pure crystal orientation (Figure 2.10 a and Table 2.1). It is because Li-ion transport was poorly in the polycrystalline structure of LN-C. Symmetric cell cycling performance (Figure 2.12e) is slightly improved for LN-C compared to bare Li but is still inferior to the plasma-treated samples due to the uneven covered surface and low ionic conductivity. Furthermore, this method took two hours which is very time consuming compared to the 2-minute plasma activation method.
Figure 2.12 Li$_3$N prepared by 2 hours of N$_2$ flow without applying plasma. (a) SEM images of LN-C as obtained. (b) Cross-sectional SEM images of LN-C. (c) SEM images of LN-C after 10 cycles at the current of 0.5 mA cm$^{-2}$ with a total capacity of 1 mAh cm$^{-2}$. d). EIS of LN-C symmetric cell before and after 50 cycles. e) Symmetric cell cycling performance of LN-C at the current of 0.5 mA cm$^{-2}$ with a total capacity of 1 mAh cm$^{-2}$. 
2.3.7 Postmortem analysis

The Li metal battery was disassembled inside the glovebox and the electrode was taken from the battery after cycling. Figure 2.13a and b show the SEM images of surface morphology of cycled bare Li electrode at low and high magnification, respectively. Needle-like Li dendrites can be identified (marked by red circles in Figure 2.13b), which forms due to the inhomogeneous surface nucleation and deposition of Li [98]. Short-circuit can happen if these dendrites penetrate the polymer separator, leading to serious safety concerns. A thick layer of dead Li is also accumulated on the bare Li surface as shown in Figure 2.13e, which may affect the mass transfer at the interface. In contrast, LN-2 exhibits a dendrite-free morphology as exhibited in Figure 2.11c and d. LN-2 protective layer is still interconnected and dense, which physically blocks the growth of Li dendrites. The Li$_3$N morphology of Li$_3$N grains is notably changed from a flower shape into a hemispherical shape after cycling. It might be caused by the deposition of fresh Li under the Li$_3$N protective layer, which swells up the Li$_3$N shells.
Figure 2.13 SEM images of bare Li after cycling at (a) low magnification and (b) high magnification. SEM images of LN-2 after cycling at (c) low magnification and (d) at high magnification. The cross-sectional view of (e) bare Li and (f) LN-2.
XRD of LN-2 was also taken after battery cycling to confirm the chemical and structure stability of the Li$_3$N layer. Strong α-phase Li$_3$N peaks reveal that its crystal structure is stable during charge and discharge (Figure 2.14). Typically, Li$_2$CO$_3$ and Li$_2$O might be detected after battery cycling due to the decomposition of the electrolyte and other side reactions. However, these peaks are not shown in XRD patterns because the dense Li$_3$N layer can block the direct contact between reactive Li and the electrolyte. Pure Li$_3$N patterns also prove that Li$_3$N is chemically stable in the electrolyte from decomposition into other materials during battery cycling.

**Figure 2.14** XRD patterns of LN-2 after 10 cycles at the current of 0.5 mA cm$^{-2}$ with a total capacity of 1 mAh cm$^{-2}$.

To better illustrate and summarize the roles played by LN-2 during plating and striping, schematic figures were created and shown in Figure 2.15. For the bare Li, at the first step
of nucleation during plating, Li tends to form small dendrites at the unevenly distributed defect spots on the surface. The Li dendrites could serve as charge centers because the charges tend to accumulate at the sharp ends [89, 90]. This causes the further growth of the Li dendrites. Likewise, in plasma-treated Li$_3$N samples, the Li$_3$N grains showed a unique flower shape and the small Li$_3$N grain tips are uniformly distributed on the surface of the electrode. These small tips are negatively charged but well distributed when the voltage is applied during the plating process. Therefore, the electrical field in Li$_3$N cells is more homogenous than that of the bare Li and leading to a more uniform Li flux. Interestingly, the Li$_3$N morphology changes into a hemispherical shape after cycling. The possible reason is the deposition of fresh Li under the Li$_3$N protective layer that swells up the Li$_3$N shells. This shape change is benign to the Li metal electrode because a spherical shape is mechanically stronger to hold the Li expansion distributing the expansion force evenly on the Li$_3$N shell.

![Figure 2.15 Schematic illustration of Li deposition and stripping of (a) bare Li and (b) Li$_3$N protected Li metal electrode.](image)
2.3.8 Full cell performance

The electrochemical performance of Li$_3$N protected Li metal was further evaluated in full cells with LiCoO$_2$ (LCO) cathode. Figure 2.16a shows the cycling performance of Li/LCO full cells at a charge/discharge rate of 1 C (1C = 0.56 mAh cm$^{-2}$, 1 hour to fully charged). The very low capacity retention of 86% is observed for bare Li/LCO full cell due to the Li loss from side reactions [45]. In comparison, the Li$_3$N artificial SEI protective layer reduces the Li loss due to the suppression of dendrite growth. The LN-2/LCO full cell demonstrates superior cycling performances with discharge capacities of 141 mAh g$^{-1}$ (1$^{st}$ cycle) and 135.5 mAh g$^{-1}$ (100$^{th}$ cycle), with a high capacity retention of more than 96%. Figure 2.16b shows the charge/discharge voltage profile at the 10th and 100th cycles. Even though bare Li and LN-2 full cells have a similar profile at the 10th cycle, the overpotential of LN-2 full cell becomes much lower than the bare Li full cell after 100 cycles. The continuous formation of unstable SEI and dead Li on the bare Li electrode could be the reasons resulting in the capacity fading and the increase of cell overpotential compared with the performance of LN-2. Meanwhile, with the help of the Li$_3$N layer, LN-2 established a strong interface and fast ion transfer channel between electrolyte and Li metal. EIS of the full cell was measured after 100 cycles and shown in Figure 2.16c. A lower charge transfer resistance was found for Li$_3$N protected LN-2, indicating a stable interface layer forms in LN-2 full cell with a reduced dead Li formation.
Figure 2.16 Full cell cycling performance. (a) Cycling performance of bare Li and LN-2 full cell at the current of 1C. (b) Charge/discharge voltage profile at the 10th and 100th cycles. (c) EIS spectra after 100 cycles.

The cycling performance of the full cells at different current rates ranging from 0.5C to 5C was conducted and shown in Figure 2.17. Even though there is no significant difference at 0.5C and 1C, LN-2 exhibits much higher capacity at 2C and 5C rates. It can be attributed to the high ionic conductivity and excellent mechanical strength, which benefited from the highly oriented Li₃N artificial Layer. This protective layer acts as a strong barrier that can suppress the formation of Li dendrites and prevent Li loss even at a high current rate. In
contrast, because of the accumulation of SEI and dead Li on the surface of bare Li, bare Li exhibits a quite low capacity at 5C current and is not able to retain the capacity when the rate decreases back to 0.5C while the capacity of LN-2 based cell can still maintain the same value compared with the initial state. The rate performance proves that LN-2 can be fast-charged and discharged in 12 minutes (5C) without capacity loss, which could provide a higher power density for electric car applications.

![Figure 2.17](image)

**Figure 2.17** Full cell rate performance of bare Li and LN-2.

LCO/LN-C full cell was also fabricated and tested to compare with bare Li and LN-2 (Figure 2.18). LN-C full cell has a first discharge capacity of 139.6 mAh g\(^{-1}\). The capacity decreases to 126.6 mAh g\(^{-1}\) after 100 cycles, which yields a capacity retention of ~90%. The performance of LN-C is slightly higher than bare Li because the thin layer of Li\(_3\)N obtained by the normal nitridation method would help to reduce the battery fading.
However, the cracks and pores in LN-C still result in the growth of Li dendrites and a capacity fading.

![Figure 2.18](image.png)

**Figure 2.18** Full cell cycling performance of LN-C.

### 2.4 Conclusions

In conclusion, a facile and efficient method to prepare the Li$_3$N artificial SEI layer was demonstrated in this chapter. The Li$_3$N layer could be in-situ formed on the Li surface after a nitrogen plasma treatment in a short time. Li dendrites were greatly suppressed due to their high modulus and high ionic conductive. In addition, the dense Li$_3$N layer covered on top of Li metal could separate the liquid electrolyte from reactive Li metal, establishing stable interphase with reduced side reactions. Consequently, Li$_3$N at an optimized N$_2$ plasma activation time of 2 minutes showed a stable depositing/stripping cycling stability to 30,000 minutes. Furthermore, a high capacity retention of 96% was also demonstrated
in the full cell with LCO as the cathode. Therefore, we anticipate this unique method by plasma activation may promote a further application for next-generation advanced lithium metal batteries.
Chapter 3 Flexible Cu-clad current collector for dendrite-free Li metal batteries

3.1 Introduction

To meet the fast-growing energy demands and develop high-energy (> 500 Wh kg\(^{-1}\)) batteries for electric vehicles and grid storage applications, researchers have explored extensive studies on batteries beyond lithium-ion (Li-ion) nowadays.[2, 14, 99-101] Among all the approaches, Li metal anode has been considered as one of the most attractive options because of its high specific capacity (3860 mAh g\(^{-1}\)) and low reduction potential (-3.04 V vs standard hydrogen electrode).[3] However, the Li metal anode is still facing problems such as large volume change, uncontrollable dendrites growth, and unstable SEI formation.[102, 103] It is well known that all these problems are correlated with each other.[4] On one hand, when Li is plated/stripped, the huge volume fluctuation breaks the fragile SEI layer and the fresh Li is exposed to the electrolyte, leading to the continuous formation of new SEI. On the other hand, the Li dendrites from uncontrollably due to the uneven Li-ion flux and SEI cracks.[104] Further, Li dendrites can be broken during

Chapter 3, in full, is a reprint of the paper “A copper-clad lithiophilic current collector for dendrite-free lithium metal anodes” as it appears in the Journal of Materials Chemistry A. Ke Chen, Rajesh Pathak, Ashim Gurung, Khan M. Reza, Nabin Ghimire, Jyotshna Pokharel, Abiral Baniya, Wei He, James J. Wu, Qiquan (Quinn) Qiao and Yue Zhou, 2020, 8, 1911-1919. Ke Chen was the primary investigator and first author of this paper.
stripping and produce “dead” Li.[105] As a result, the formation of a thick SEI layer and dead Li consume a large amount of fresh Li and electrolyte, leading to a low Coulombic efficiency (CE) and fast battery failure.[17] Therefore, to efficiently accommodate volume changes and avoid dendrite growth need to be accomplished in order for commercializing Li metal anode in the next-generation batteries.

Considerable efforts have been devoted to stabilizing Li metal anode. One of the strategies is to create an in-situ robust SEI layer by introducing electrolyte additives such as LiNO$_3$, CsPF$_6$, and AlCl$_3$,[70, 106, 107] or develop an ex-situ artificial SEI layer such as Li$_3$N, carbon nanospheres, and Al$_2$O$_3$.[35, 40, 41, 108] Employing new electrolytes such as dual-salt LiDFOB/LiBF$_4$ electrolyte also can be a potential way to improve the performance of Li metal batteries.[109] Although these methods can suppress dendrite growth to some extent, they cannot sufficiently avoid large volume changes during the Li plating/stripping process. The use of a porous current collector as the host for Li metal has been demonstrated as a promising approach because it can accommodate the large Li volume change and stabilize the SEI layer. Most importantly, the high surface area reduces the local current density that quenches the Li dendrite growth.

For the Li metal battery, the Li-ion concentration is relatively steady at a low current density. However, at higher current density, the cations will be rapidly consumed in the vicinity of the negative electrodes with a sharp concentration depletion.[19] This leads to a local space charge with a strong negative electric field, it will electroabsorb and electroplate massive Li ions in a short period, resulting in the formation of dendrites on the Li metal anode surface.[3, 20, 21] This behavior for dendrite growth is known as Sand’s behavior as widely reported in the literature.[26, 49, 50] The Sand’s time equation
(Equation 1) describes that the initiation time of dendrite growth ($\tau$) is significantly affected by the applied current density $J$, where $J$ is effective electrode current density, $D$ is the ambipolar diffusion coefficient, $e$ is the electronic charge, $C_0$ is initial Li salt concentration, and $t_a$ is anionic transference number.[51] Compare to the planar current collector, the 3D current collector has a much higher surface area, which reduces the local current density of the Li metal anode, thus mitigate the dendrite growth. Similarly, the Li dendrite growth rate ($V_{tip}$) is also found to be reduced at a lower current density $J$ (Equation 2), where $V$ is molar volume and $F$ is Faraday’s constant.[52] In addition, submicron-ranged structures in the 3D current collector induce a homogenous charge distribution, eventually leading to a relatively even Li deposition.[53]

$$\tau = \pi D \left( \frac{eC_0}{2Jt_a} \right)^2$$  \hspace{1cm} (3.1)

$$V_{tip} = \frac{IV}{F}$$  \hspace{1cm} (3.2)

Various porous metal hosts such as nickel and copper foams [28, 55, 110-114] have been used to extend the lifetime of Li metal anode due to their high surface area and lithiophility. However, most of the previously reported metal scaffolds were stiff with little mechanical flexibility, and therefore they cannot effectively embrace the large volume changes of Li anode after Li deposition. Moreover, metal scaffolds often have a high volumetric mass density which significantly reduces the energy density of full cells in practical application [115]. For example, copper has a density of 8.96 g cm$^{-3}$, which is much higher than polymer or carbon at less than1 g cm$^{-3}$[116].

Herein, we report a novel 3D light-weight and flexible copper-clad carbon framework (CuCF) that meet all the desirable properties including high stability and scalability for Li
metal anode. This CuCF was simply fabricated via pyrolysis of melamine-formaldehyde foam (MF) followed by Cu electroplating. Instead of using high density pure metal-based current collector, a thin layer of Cu is deposited on the light-weight carbon fiber backbone to achieve a higher energy density. As a large surface area 3D interconnected structure, the flexible CuCF can significantly reduce the local current density and accommodate the volume changes during Li plating/stripping cycles. In CuCF, more uniform Li nucleation sites were induced to achieve a dendrite free-Li metal anode due to a unique wrinkle Cu surface. A high CE of more than 99.5% was maintained after 300 cycles (~1200 hours) at the current density of 0.5 mA cm\(^2\). The Li@CuCF symmetric cell showed a highly stable cycling performance at a high current density of 5 mA cm\(^2\) for more than 170 cycles.

3.2 Experimental

3.2.1 Preparation of CF

Melamine-formaldehyde foam (MF, BASF Corp.) was cut into 5 mm thin pieces and then carbonized in a tube furnace for two hours at 900 °C under N\(_2\) atmosphere, with a temperature increase rate of 10 °C/min. After cooling down to room temperature, the obtained CF was washed with deionized (DI) water and ethanol several times to remove the residual contaminants, and then dried in a vacuum oven at 80 °C.

3.2.2 Preparation of CuCF

CuCF was prepared by the electroplating method. As shown in Figure 3.1, a pure Cu foil anode and CF cathode are immersed in the 1 M CuSO\(_4\) electrolyte solution. A pulse current of 10 mA cm\(^2\) was applied to the circuit using Biologic VSP potentiostat (15-second electroplating followed by 10-second rest). During electroplating, Cu was dissolved from
the Cu anode and deposited on to CF. After a specific amount of Cu plating time, CuCF was washed with DI water and ethanol and then dried in a vacuum oven at 80 °C.

![Experiment setup of Cu electroplating](image)

**Figure 3.1** Experiment setup of Cu electroplating. (a) Schematic of Cu plating on carbon foam. (b) Photo of the experiment setup.

### 3.2.3 Optimization of Cu electroplating time

Cu loadings of CuCF can be varied by controlling the Cu coating time, CE test was also carried out accordingly. The CuCF obtained at 2, 4, 6, and 8 minutes are named as CuCF-2, CuCF-4, CuCF-6, and CuCF-8, respectively. At lower electroplating time (2 and 4 minutes), copper was found to form particles on the surface of carbon fibers with a non-continuous Cu coating layer (Figure 3.2 a-d). This non-uniform Cu coating leads to an early failure of the battery (Figure 3.2i), which might because the Cu particles can induce an uneven Li nucleation site and accelerate the dendrite growth. The CuCF-6 shows a uniform copper coverage with a thin Cu layer (Figure 3.2 e and f). At a longer deposition time (8
minutes), the Cu layer thickness increases significantly because of the high conductivity of the pre-deposited Cu (Figure 3.2 g and h). Although CuCF-8 shows a similar cycling performance to CuCF-6, the increased Cu loading might decrease the battery energy density. Therefore, CuCF-6, which has optimized coating layer thickness and less process time, was selected to study the electrochemical performance in this chapter. Hereafter, CuCF will be used to refer to CuCF obtained at 6-minute electroplating (CuCF-6) unless otherwise indicated. The parameters of CuCF obtained at different electroplating time were summarized in Table 3.1.
Figure 3.2 Optimization of Cu electroplating time. SEM images of CuCF with the electroplating time of (a and b) 2 minutes, (c and d) 4 minutes, (e and f) 6 minutes, and (g and h) 8 minutes. (i) CE cycling test of CuCF at different electrodeposition times.

Table 3.1 Summary of CuCF obtained at different Cu electroplating times.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Total time (second)</th>
<th>Effective electroplating time (second)</th>
<th>Average weight (mg)</th>
<th>Cu loading density (mg/cm$^2$)</th>
<th>Cycling number at CE &gt; 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>-</td>
<td>-</td>
<td>0.50</td>
<td>-</td>
<td>123</td>
</tr>
<tr>
<td>CuCF-2</td>
<td>200</td>
<td>120</td>
<td>0.92</td>
<td>0.24</td>
<td>161</td>
</tr>
<tr>
<td>CuCF-4</td>
<td>400</td>
<td>240</td>
<td>1.47</td>
<td>0.55</td>
<td>174</td>
</tr>
<tr>
<td>CuCF-6</td>
<td>600</td>
<td>360</td>
<td>2.10</td>
<td>0.91</td>
<td>&gt;200</td>
</tr>
<tr>
<td>CuCF-8</td>
<td>800</td>
<td>480</td>
<td>2.71</td>
<td>1.25</td>
<td>&gt;200</td>
</tr>
</tbody>
</table>

*Pulse current was applied with 15s of electroplating and 10s of rest for each cycle.
3.2.4 Characterization

3.2.4.1 SEM and XRD

The detailed experiment steps for SEM and XRD have been discussed in Chapter 2. SEM images of CF and CuCF before and after Li plating were taken using a Hitachi 4700 scanning electron microscope. A sealed container was used while transferring the sample from the glove box to the SEM chamber. X-ray diffraction (XRD) was conducted using a Rigaku SmartLab diffractometer.

3.2.4.2 Raman spectroscopy

Horiba Raman system was used for Raman spectroscopy. 532 nm laser was used and the scattered signal from the sample was collected at the range from 1000 to 2000 cm\(^{-1}\).

3.2.4.3 Brunauer-Emmett-Teller (BET) surface area

The specific surface area was measured by ASAP 2460 Surface Area and Porosimetry Analyzer. After the sample was degassed at 350 °C, the absorption/desorption of the samples was performed using the following steps: Absorption Isotherm BET p/po 0.05 to 0.3 with 0.025 steps (11 data points); Absorption Isotherm BJH p/po 0.5 to 0.995 using the geometric approach to saturation (14 data points); Desorption Isotherm BJH p/po 0.995 to 0.1 using the geometric approach to saturation (20 data points).

3.2.5 Electrochemical measurements.

3.2.5.1 CE test.

The coin cells (CR2032) were assembled in an argon glovebox (Mbraum, O\(_2\) and H\(_2\)O level < 0.1 ppm) for all the electrochemical measurements. For the coulombic efficiency test,
planar Cu (MTI corp.), commercial Cu foam (MTI corp.), CF or CuCF was used as the working electrode and Li metal was used as the counter electrode with Celgard 2500 film as the separator. The electrolyte was 1M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma Aldrich) in 1,3-dioxolane (DOL, Sigma Aldrich)/1, 2-dimethoxyethane (DME, Sigma Aldrich) (1:1 volume ratio) with 1 wt% Li nitrate (LiNO₃, Alfa Aesar). The amount of electrolyte used was controlled as ~50 uL for each cell. Li was first plated onto the current collector and then stripped until the voltage exceeding the cutoff voltage of 0.5 V. Cells were tested under a different current density of 0.5 and 1 mA cm⁻² with the capacity of 1 or 2 mAh cm⁻² using Land battery analyzer (CT2001A).

3.2.5.2 Symmetric cell test.

For the preparation of Li@planar Cu, Li@CF, and Li@CuCF electrodes, 4 mAh/cm² of Li were pre-deposited on planar Cu, CF, and CuCF, respectively in the coin cell at a current density of 0.5 mA/cm². After the cells were disassembled, the pre-deposited Li electrodes were rinsed in DOL/DME (1:1 v/v ratio) to remove the extra Li salts, and dried in the Ar glovebox. The obtained Li@planar Cu, Li@CF, and Li@CuCF were used further for the test of symmetric cells and Li/ lithium iron phosphate (LFP) cells according to previous reports. [26, 49, 50, 117-120] Symmetric cells were cycled at the current density of 5 mA cm⁻² with a capacity of 1 mAh cm⁻².

3.2.5.3 Full cell test.

For making LFP cathode, a slurry containing LFP, Super P carbon, and polyvinylidene fluoride (PVDF) (80:10:10 weight ratio) were prepared in N-Methyl-2-pyrrolidone (NMP) solvent. The slurry was coated on aluminum foil and then dried in a vacuum oven for 12
hours. Li/LFP cells were cycled at the voltage range between 2.5 and 4.2 V at 1C. The electrolyte was 1M LiFP₆ in the mixture of ethylene carbonate (EC) / dimethyl carbonate (DEC) (1:1 volume ratio) (Sigma Aldrich).

3.2.5.4 EIS test.

Electrochemical impedance spectroscopy (EIS) was carried out by Biologic VSP potentiostat with frequency ranging from 0.1Hz to 100K Hz.

3.2.5.5 Conductivity measurement.

The conductivity measurement, linear sweep voltammetry was conducted at a scan rate of 100 mV/s between -0.5V and +0.5V on the coin cell with only two spacers, two spacers with CF or CuCF in between.

3.3 Results and discussion

3.3.1 Morphology and chemical composite analysis

SEM images of the CF and CuCF are shown in Figure 3.3. The carbon fibers in CF having a diameter of ~ 2 µm are interconnected and form a cross-linked skeleton (Figures 3.3 a and b). The empty spaces between fibers are range from 30 -100 µm, which makes CF a very low mass to volume density. The average weight for one piece of CF electrode (diameter of 15 mm) is measured to be 0.5 mg. After the Cu coating, CuCF shows a very similar porous structure to CF (Figure 3.3d, e, h, and i). The average weight for the CuCF electrode is increased to 2.1 mg, given the Cu loading density of 0.91 mg cm⁻². The wide spaces of CF and CuCF provide them easy access to the electrolyte with reduced mass transfer resistance in batteries[121]. Figure 3.3c shows an enlarged SEM image of a single
carbon fiber that has a smooth surface. In comparison, CuCF fibers (Figure 3.3e and f) become much rougher after Cu coating. This special morphology and structure could offer more Li nucleation sites and increase the Li metal attachment to the fiber surface during Li plating [118]. Figure 3.3g shows a cross-sectional SEM of a single CuCF fiber. The Cu coating layer on Cu can be found to be very uniform with an average diameter of ~200 nm.

**Figure 3.3** SEM images of (a) CF, (b) single CF fiber, and (c) magnification of single CF fiber. SEM images of (d) CuCF, (e) single CuCF fiber, and (f) magnification of single CuCF fiber. (g) Cross-sectional SEM image of a single CuCF fiber. SEM of CuCF at (h) top and (i) cross-sectional view.
Figure 3.4a shows the nitrogen adsorption-desorption isotherms plots of CF and CuCF. The BET specific surface area of CF and CuCF are 624.7 and 470.6 m$^2$/g, respectively, which are much higher than a 2D planar current collector. The increased surface area could significantly reduce the local current density at the electrode and suppress the dendrite formation. Even though the average weight of CuCF current collector is 4 times higher than that of CF, the specific surface area of CuCF is only decreased from 624.7 to 470.6 m$^2$/g, it can be attributed to the unique surface Cu decoration which not only increased the conductivity but also the surface area.

The XRD pattern shows that the CF (Figure 3.4b) has a broad (002) peak at ~20° indicating a typical low graphitization structure. After Cu coating, the XRD pattern of CuCF exhibits high-intensity peaks of (111), (200), and (220) at 43.4°, 51.5°, and 74.3° (PDF#65-9743), respectively. This supports that a highly crystallized Cu was obtained.[122] Raman spectra of the control CF (Figure 3.4c) and its fitted curve show D and G bands at 1350 and 1580 cm$^{-1}$, respectively. The D band is related to defective/disordered structure, while the G band is for graphite sheets.[123, 124] The integrated area ratio between the G band and D band is 0.76, indicating a low graphitization level [125], which is consistent with XRD results. The conductivity of both CF and CuCF was measured by calculating the slope of their I-V curve (Figure 3.4d). With Cu coating, the conductivity of CuCF has improved two orders of magnitude than CF from 4.32×10$^{-4}$ S·cm$^{-1}$ to 1.38×10$^{-2}$ S·cm$^{-1}$. 
Figure 3.4 (a) Nitrogen adsorption-desorption isotherms plots of CF and CuCF. (b) XRD patterns of the CF and CuCF (inset: enlarged XRD patterns between 15 and 35°). (c) Raman spectra of the CF. (d) The conductivity measurement of CF and CuCF.

3.3.2 Li deposition behavior on different current collectors

4 mAh cm⁻² of Li was deposited onto planar Cu, CF, and CuCF current collectors at a deposition current density of 0.5 mA cm⁻¹ to investigate lithiophilicity of different current collectors and corresponding Li morphology after plating. Figure 3.5 shows the Li plating voltage profiles of planar Cu, CF, and CuCF. Typically, a voltage dip and a plateau can be
found in the profiles and the voltage difference between them is defined as nucleation overpotential which is also known as the Li nucleation barrier. \cite{126} The lower nucleation overpotential, the higher lithiophilicity of the current collector is, which further enhances a dendrite-free Li plating. \cite{127} The planar Cu shows a high nucleation overpotential of 150 mV, indicating a significantly large energy barrier when Li is plated on its surface. For CF, a small discharging slope with a lower nucleation overpotential of 47.1 mV is observed because the intercalation reaction between Li and carbon occurred. The small discharging slope is commonly found in the carbon-based Li host. \cite{61, 125, 127-130} The intercalation reaction product (LiC₆) contributes to a higher lithiophilicity in CF than that in the planar Cu. \cite{126, 129} The CuCF shows the highest lithiophilicity with the lowest nucleation overpotential of 29.0 mV. This can be attributed to enhanced surface conductivity and numerous nucleation sites on the surface of the CuCF after copper cladding. \cite{115}

![Figure 3.5 Voltage profiles of Li plating on Planar Cu, CF, and CuCF.](image-url)
Ex-situ SEM was conducted at different plating stages (e.g., 1, 2, and 4 mAh cm\(^2\)) to inspect Li morphology and its revolution on the current collectors. Fibrous Li starts to grow on the surface of the planar Cu at 1 mAh cm\(^2\) (Figure 3.6a) and becomes longer and thicker at a higher capacity of 2 and 4 mAh cm\(^2\) (Figure 3.6 b and c). It is due to the random Li nucleation on the surface of the Cu foil and the uncontrollable growth thereafter. For CF, at the beginning stage of the Li deposition, Li does not cover the entire surface of carbon fibers and nucleates as micrometer-ranged particles (Figure 3.6d). When the Li deposition capacity increases, Li keeps depositing on the nucleation sites and further grow into long fibrous dendrites at 2 and 4 mAh cm\(^2\) (Figure 3.6 e and f). As expected, CuCF shows a much different Li morphology than planar Cu and CF, CuCF fibers show a smooth Li coverage due to well-distributed Li nucleation sites on the fiber surface at the capacity of 1 mAh cm\(^2\) (Figure 3.6g). At a larger Li deposition capacity (2 mAh cm\(^2\)), Li tends to grow bigger and fills in the space between the CuCF fibers (Figure 3.6h). Even at the capacity of 4 mAh cm\(^2\), no Li dendrite was found on the surface (Figure 3.6i). For practical applications of Li metal anode, a dense/large nodule size Li plating with a smooth surface is required. The dendrite-free and lower surface area Li metal after plating could reduce side reactions by decreasing the unnecessary contact between Li and electrolyte during the battery cycles.[2]
Figure 3.6 The morphology of plated Li on planar Cu at the capacity of (a) 1 mAh cm\(^{-2}\), (b) 2 mAh cm\(^{-2}\), and (c) 4 mAh cm\(^{-2}\), CF at (d) 1 mAh cm\(^{-2}\), (e) 2 mAh cm\(^{-2}\), and (f) 4 mAh cm\(^{-2}\), and CuCF at (g) 1 mAh cm\(^{-2}\), (h) 2 mAh cm\(^{-2}\), and (i) 4 mAh cm\(^{-2}\).

SEM images after Li stripping was also taken. In planar Cu, fibrous dendrites tend to break and become inactive dead Li during the stripping process (Figure 3.7a), resulting in a low CE and short cycling life. CF shows less dead Li, but some residual Li particles can still be found on the carbon fiber surface (Figure 3.7b) because of the breakdown of dendrites and the formation of a non-smooth fiber surface. The CuCF exhibits a smooth surface without any residual Li particles (Figure 3.7c), which is comparable to the original CuCF before plating (Figure 3.3a). The high reversibility of Li plating/stripping of CuCF could lead to a high Li utilization efficiency and a better battery performance.
Figure 3.7 SEM images of (a) planar Cu, (b) CF, and c) CuCF after Li stripping.

Figure 3.8 shows the schematic for different Li deposition behaviors on planar Cu, CF, and CuCF. Uneven charge accumulation typically occurs on the protrusions/defects of the planar copper foil due to the “tip effect”.\cite{53} This leads to a faster Li deposition on the protrusions/defects of the copper foil and facilitates the Li dendrite growth (Figure 3.8 a, b, and c).\cite{131} Even though 3D structured current collectors have been proven to be more favorable for Li deposition, they display different Li plating behaviors due to their unique composite and surface properties. Both CF and CuCF have a 3D cross-linked structure before Li deposition (Figure 3.8 d and g), however, their electron distributions are different during plating due to the different conductive features. In CF, the conductivity is lower and electron distribution is not uniform due to its low graphitization level. Electrons mainly accumulate at the highly conductive spots, where Li first nucleates (Figure 3.8 e). With the increase of deposition time, Li preferentially deposits at these nucleation sites and causes rapid growth of Li dendrites at larger capacity (Figure 3.8 f). Furthermore, the uneven Li deposition along with an unstable SEI formation accelerates Li dendrite growth.\cite{102} Consequently, a lower CE and higher cell overpotential occur due to the dead Li accumulation and electrolyte drying-up. In the case of CuCF, the electrons are
homogeneously distributed on the surface of CuCF fibers due to the highly conductive uniform Cu cladding (Figure 3.8 h). Moreover, the nanostructured Cu decoration increases its Li adhesion and provides more Li nucleation sites. This helps to form a thin but uniform Li layer on the CuCF fiber surface. This Li layer then grows thicker at higher deposition capacity until Li fulfills the CuCF void (Figure 3.8i). Therefore, the dendrite-free Li deposition promotes a high CE at each cycle.
3.3.3 Comparison with commercial Cu foam.

To compare the performance of the CuCF with the commercially available Cu foam, Cu foam was purchased from MTI Corp, which is widely used in battery or supercapacitor anode substrate/current collector. As shown in Figure 3.9a, the commercial Cu foam may be folded but cannot resume its initial shape after the bent. SEM images show that the
diameter of the Cu fibers in C foam is ~100 µm which is much higher than that of CuCF (~1 µm) (Figure 3.9b). At a large magnification (Figure 3.9b), the surface of the Cu foam had a similar surface to Cu foil. The Li morphology after plating on commercial Cu foam was also studied. Dendrites were found to form at all plating stages because of its poor lithiophilicity and relatively low specific surface area.[112]

![Figure 3.9 SEM images of commercial Cu foam (a) at low magnification and (b) high magnification. (c) Digital photo of commercial Cu foam after bending. SEM images of commercial Cu foam after Li deposition with the capacity of (a) 1, (b) 2, and (c) 4 mAh cm\(^{-2}\).]

3.3.4 Coulombic efficiency study.

For the CE test, CuCF maintains a high CE of 99.5% after 300 cycles (~1200 hours) at a current density of 0.5 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\) (Figure 3.10 a). This high CE can be attributed to the dendrite-free Li deposition on CuCF with reduced side reactions between Li and electrolyte. In contrast, the planar Cu shows a rapid CE decrease after only 80 cycles. The CF also shows a cycling life of only around 120 cycles with a CE decrease
to ~50%. The decrease of CE in planar Cu and CF is caused by the continuous formation of inactive dead Li when Li dendrites break down into electrically isolated Li. Figure 3.10b shows the comparison of charge/discharge profiles between CF and CuCF at the 150th cycle. CuCF has a lower voltage hysteresis than CF, which confirms the favorable Li nucleation and plating on the CuCF. The CE of CuCF is compared with some similar approaches to Li metal battery current collector study, CuCF shows the superior performance among the state of the art work (Table 3.2). The CE tests were also conducted at the higher current and higher capacity of 1 mA cm$^{-2}$ with the capacity of 1 mAh cm$^{-2}$ (Figure 3.10c), and at 1 mA cm$^{-2}$ with the capacity of 2 mAh cm$^{-2}$ (Figure 3.10e). Three different current collectors display a similar phenomenon as at the lower current. Though the CF shows slightly improved cycling stability than planar Cu, the CE still decreases after 100 cycles (1 mA cm$^{-2}$ / 1 mAh cm$^{-2}$) and 70 cycles (1 mA cm$^{-2}$ / 2 mAh cm$^{-2}$), respectively. Notably, the CuCF exhibits a high CE larger than 98% at the current density of 1 mA cm$^{-2}$ and a capacity of 2 mAh cm$^{-2}$. Figure 3.10 d and f show the corresponding Li plating/stripping voltage profiles at the 150th and 80th cycle, respectively. CuCF exhibits a lower voltage hysteresis than planar Cu and CF.
Figure 3.10 (a) Coulombic efficiency of planar Cu, CF, and CuCF at the current density of 0.5 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\), (c) at the current density of 1 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\), and the current density of 1 mA cm\(^{-2}\) with the capacity of 2 mAh cm\(^{-2}\). The corresponding plating/stripping voltage profiles at the (b) 150th cycle, (d) 150th cycle, and (f) 80th cycle, respectively.
### Table 3.2 Summary of the Coulombic efficiency of similar works.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Li host</th>
<th>Current density (mA/cm²) / Capacity (mAh/cm²)</th>
<th>Cycle Number / CE after cycling</th>
<th>Electrolyte / Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adv. Funct. Mater. 2019, 29, 1808468[26]</td>
<td>3D Porous Cu current collectors derived by hydrogen bubble dynamic template</td>
<td>0.5 / 1 / 1</td>
<td>250 / 98%</td>
<td>1 M LiTFSI in DOL/DME with 2 wt% LiNO₃ / (60µL)</td>
</tr>
<tr>
<td>Adv. Energy Mater. 2018, 1703404[50]</td>
<td>Vertically aligned CuO nanosheet grown on planar Cu</td>
<td>0.5 / 1</td>
<td>180 / 94%</td>
<td>1 M LiTFSI in DOL/DME with 1 wt% LiNO₃ / (40 µL)</td>
</tr>
<tr>
<td>Energy Storage Materials 11 (2018) 127-133[132]</td>
<td>3D pie-like Cu nanowires wrapped by graphene</td>
<td>1 / 2</td>
<td>120 / ~97%</td>
<td>1 M LiTFSI in DOL/DME with 1 wt% LiNO₃ / (not mentioned)</td>
</tr>
<tr>
<td>Adv. Energy Mater. 2018, 1800914[55]</td>
<td>N-Doped graphene modified 3D porous current collector</td>
<td>0.5 / 1 / 1</td>
<td>150 / 97.5%</td>
<td>1 M LiTFSI in DOL/DME with 1 wt% LiNO₃ / (70 µL)</td>
</tr>
<tr>
<td>Angew. Chem. Int. Ed. 2017, 56, 7764–7768[61]</td>
<td>N-Doped graphene matrix</td>
<td>1 / 1 / 1</td>
<td>200 / 98%</td>
<td>1 M LiTFSI in DOL/DME with 5 wt% LiNO₃ / (not mentioned)</td>
</tr>
<tr>
<td>This work</td>
<td>Flexible 3D CuCF</td>
<td>0.5 / 1 / 1</td>
<td>300 / 99.5%</td>
<td>1 M LiTFSI in DOL/DME with 1 wt% LiNO₃ / (50 µL)</td>
</tr>
</tbody>
</table>
Figure 3.11 shows SEM images of planar Cu, CF, and CuCF after 100 cycles at the current density of 0.5 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\). A very thick layer of dead Li can be noticed covering all over the planar Cu surface (Figure 3.11a), which is the reason for its rapid CE dropping. Similarly, large chunks of dead Li can also be found on CF after 100 cycles because of dendrite breakdown (Figure 3.11b). For CuCF, a very smooth Li surface was observed without any Li dendrites on the surface (Figure 3.11c).

![SEM images of planar Cu, CF, and CuCF after 100 cycles at the current density of 0.5 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\).](image)

**Figure 3.11** The SEM images of (c) planar Cu, (d) CF, and (e) CuCF after 100 cycles at the current density of 0.5 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\).

### 3.3.5 High capacity and charging rate performance of CuCF

To prove the CuCF can work at both low and high capacity, CE was tested under the current of 1 mA cm\(^{-2}\) with different capacities of 1, 2, 4, and 8 mAh cm\(^{-2}\) (Figure 3.12 a). The changing of capacity does not affect the CE even at the capacity of 8 mAh cm\(^{-2}\), indicating CuCF can be used for very high capacity applications. Figure 3.12 b shows the voltage profile at different capacities. The plating curve is flat and no increase of voltage is found during high capacity plating, which proves that the fresh plated Li is well accommodated into the CuCF. The CE test was conducted at a higher current of 2 mA cm\(^{-2}\) with a capacity of 8 mAh cm\(^{-2}\) (Figure 3.12 c). A high CE of more than 96% was obtained for CuCF. Both
planar Cu and CF failed earlier than CuCF, which is due to the dendrite growth at a higher capacity. The fact that CuCF can work both at high current and high capacity gives it a great potential application in fast-charging electric vehicles.

Figure 3.12 (a) Coulombic efficiency test of CuCF at the current of 1mA cm\(^{-2}\) with capacity 1, 2, 4, and 8 mAh cm\(^{-2}\). (b) The corresponding plating/stripping voltage profiles at different capacities. (c) Coulombic efficiency test of planar Cu, CF, and CuCF at the current of 2 mA cm\(^{-2}\) with the capacity of 8 mAh cm\(^{-2}\).
The SEM images of Li@CuCF at 4 mAh cm$^{-2}$ have been illustrated in Figure 3.6i with a higher magnification. In order to have a better view of how the Li is distributed, Figure 3.13 a low magnification SEM image. There is still plenty of space in the CuCF to host more Li. SEM images of Li plating to the capacity at 8 and 16 mAh cm$^{-2}$ are shown in Figure 3.13 b and c. All the Li was found to be constrained inside the framework without dendrites formation. With further Li deposition, space can be filled up at the capacity of 16 mAh cm$^{-2}$ without Li dendrite formation. From the cross-sectional SEM images (Figure 3.13 d, e, and f), the thickness can be measured after Li deposition. The thickness is much lower than that showing in Figure 3.3i because of the pressure applied in the coin cells. Although the capacity was increased 4 times from 4 mAh cm$^{-2}$ to 16 mAh cm$^{-2}$, the increase in the thickness of deposited Li was only two times (from ~70 µm to ~150 µm) indicating an adjustable thickness due to the flexibility. The volumetric and gravimetric capacity at the capacity of 4 mAh cm$^{-2}$, 8 mAh cm$^{-2}$, and 16 mAh cm$^{-2}$ were then calculated accordingly and summarized in Table 3.3. The CuCF has a very high gravimetric capacity of 3001.1 mAh g$^{-1}$ at 16 mAh cm$^{-2}$, which has reached 77.7 % of the theoretical value of Li metal anode (3860 mAh g$^{-1}$). This can be attributed to the ultra-lightweight of the CuCF.
Figure 3.13 Surface SEM images of Li@CuCF at the areal capacity of (a) 4 mAh cm\(^{-2}\), (b) 8 mAh cm\(^{-2}\), and (c) 16 mAh cm\(^{-2}\). Cross-sectional SEM images of Li@CuCF at (d) 4 mAh cm\(^{-2}\), (e) 8 mAh cm\(^{-2}\), and (f) 16 mAh cm\(^{-2}\).

Table 3.3 Summary of the volumetric and gravimetric capacity of Li@CuCF

<table>
<thead>
<tr>
<th>Areal Capacity /mAh cm(^{-2})</th>
<th>Volumetric Capacity /mAh cm(^{-3})</th>
<th>Gravimetric Capacity /mAh g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>571.4</td>
<td>1795.1</td>
</tr>
<tr>
<td>8</td>
<td>888.9</td>
<td>2453.8</td>
</tr>
<tr>
<td>16</td>
<td>1066.7</td>
<td>3001.1</td>
</tr>
</tbody>
</table>

Symmetric cells were assembled using Li@planar Cu, Li@CF, or Li@CuCF, in which 4 mAh cm\(^{-1}\) of Li was pre-deposited. The symmetric cells were then measured at a high...
current density of 5 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\). Li@CuCF exhibits a stable cycling profile up to 170 cycles (Figure 3.14a). It also shows a smooth plating/stripping profile and low voltage hysteresis compared to Li@planar Cu and Li@CF (Figure 3.14 b and c). In comparison, Li@planar Cu and Li@CF have either fluctuated or increased voltage profiles with a low cycling life of fewer than 50 cycles. The reason is that both planar Cu and CF suffer from dendrite growth and breakdown that cause dead Li accumulation. The voltage profiles at the 1st and 50\(^{th}\) cycle were magnified (Figure 3.14b and c). CuCF has a flat plating/stripping voltage curve with a much lower overpotential, indicating its low mass transfer resistance.[121]
Figure 3.14 (a) Symmetric cell cycling performance at the current of 5 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\) for Li@ planar Cu, Li@ CF, and Li@ CuCF. The corresponding plating/stripping voltage profile at the (b) 1st and (c) 50th cycle.

3.3.6 Flexibility study of CuCF

The flexibility test was conducted by comparing the structure and electrochemical performance differences before and after 100 times folding of the CuCF electrode. The as-prepared CuCF electrode was folded as indicated in Figure S3.15a and b. The CuCF can easily recover to its original shape by itself after the pressure was released, showing excellent mechanical flexibility (Figure 3.15c). In comparison, commercial Cu foam may
be folded but cannot resume its initial shape after bent (Figure 3.9a). Even after 100 times folding, there is no significant change was found for CuCF (Figure 3.15 d & e). CuCF was also examined by SEM after folding 100 times. It is still cross-linked without any structural change (Figure 3.15 f and g). Even s small amount of CuCF fibers are found broken at the folding area but it is believed not to affect the battery cycling performance as the EIS and CE test results.

The EIS can be used to evaluate the electrode resistance and battery impedance while operating. The EIS curve of CuCF before and after folding shows almost the same serials resistance and charge transfer resistance, indicating that the folding does not affect the electronic performance of CuCF (Figure 3.16a). CE cycling test was also performed at the current density of 1 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\) for both samples with and without a folding test (3.16b). Two CE curves are identical with no significant differences after 200 cycles. The data are also consistent with the cycling test data presented in Figure 3.10c.
Figure 3.15 The digital photos of (a) CuCF, (b) folded CuCF, (c) self-recovered CuCF after folding, (d) CuCF after 50 times folding, and (e) CuCF after 100 times folding. SEM images of (f) CuCF and (g) CuCF after 100 times folding.

Figure 3.16 (a) EIS spectra and (b) CE cycling test of CuCF without folding and after 100 times folding at the current density of 1 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$. 
3.3.7 Full cell performance

To further evaluate the practical application of CuCF, cells with pre-deposited Li@CuCF as anode and LiFePO₄ (LFP) as a cathode were studied at a current of 1C. Li@CuCF shows a stable cycling performance up to 200 cycles with a negligible capacity decrease (Figure 3.17a). The 1st and 200th discharge capacity of CuCF full cell is 122.2 and 121.6 mAh g⁻¹, respectively, giving high capacity retention at 99.5%. However, for Li@planar Cu, it exhibits a continuous capacity fading due to continuous Li loss during Li plating/stripping cycles[125]. Li@CF has a better cycling performance than Li@planar Cu but it still has a low Li utilization. The charge/discharge curves at the 10th and 100th cycles are displayed in Figure 3.17b and c. Even though all three current collectors have a similar voltage profile at the initial cycles, the overpotential increases much more significantly for Li@planar Cu and Li@CF than Li@CuCF after 100 cycles. This could be attributed to the dead Li accumulation in Li@CF and Li@planar Cu full cells, which hinders the Li ion transfer at the interface of the electrode. Interestingly, the Li@CF shows a different charge/discharge curve pattern after 100 cycles with a much lower discharge plateau. This might due to the Li insertion reaction with the amorphous carbon material in CF after Li was fully consumed. The reaction potential between Li and amorphous carbon (~0.3 V vs Li/Li⁺) is higher than Li deposition potential (0 V vs. Li/Li⁺) [129].
Figure 3.17 (a) Full cell cycling performance of Li@planar Cu, Li@CF, and Li@CuCF at 1C. (b) Charge/discharge profile at the 10th cycle and (c) 100th cycle.

The EIS was performed before cycling and at the 100th cycle (Figure 3.18 a and b). All Li@planar Cu, Li@CF, and Li@CuCF show a comparable charge transfer resistance at the beginning cycles. However, the Li@planar Cu and Li@CF exhibit a larger charge transfer resistance after 100 cycles due to the dead Li build-up at the interface between the active Li electrode and liquid electrolyte. In comparison, the charge transfer resistance of Li@CuCF keeps almost the same throughout the cycling because of the stable SEI formation on the surface of the electrode, benefiting from the dendrite-free deposition in
CuCF. The EIS results are consistent with full cell cycling performance, in which Li@CuCF exhibits much higher cycling stability than CF and planar Cu samples.

**Figure 3.18** EIS of planar Cu, CF, and CuCF full cell before cycling and at the 100th cycle.

Fast-changing/discharging ability is one of the most important properties in practical application for batteries. The full cells are tested under different current ranges from 0.2C (fully charged in 5 hours) to 5C (fully charged in 12 minutes) (Figure 3.19). Li@planar Cu, Li@CF, and Li@CuCF deliver a comparable capacity at the lower current density of 0.2C, 0.5C, and 1C. However, Li@planar Cu and Li@CF exhibit a lower capacity than Li@CuCF at 2C and 5C. Specifically, the Li@planar Cu shows a near-zero capacity because of its low Li utilization. In contrast, a highly conductive skeleton of CuCF enables a reduced local current density and lower mass transfer resistance even at a high rate, which leads to a higher capacity. Besides, Li@CuCF also recovers almost 100% of capacity after
returning to 0.5C from 5C, which is attributed to its stable dendrite-free Li plating/stripping with a negligible Li loss.

![Graph showing rate performance of Li@planar Cu, Li@CF, and Li@CuCF full cell.](image)

**Figure 3.19** Rate performance of Li@planar Cu, Li@CF, and Li@CuCF full cell.

### 3.4 Conclusions

In summary, a flexible 3D porous CuCF using carbon fiber as backbone and Cu as the coating layer was fabricated as the current collector for Li metal anode via a facile method. The obtained nanostructured Cu decorated CuCF has a higher conductivity and larger surface area, leading to a uniform, dendrite-free Li plating/stripping. In addition, the 3D nanostructured CuCF can accommodate the different amounts of Li due to its adjustable thickness and mechanical flexibility. The SEI layer also can be further stabilized because of the smooth and compact Li deposition. A high CE of 99.5% was demonstrated after 300
cycles (~1200 hours). Even at a high current density of 5 mA cm$^{-2}$, the CuCF still lasted for 170 cycles. This work demonstrates that the flexible 3D CuCF current collector provides a promising approach to achieve a dendrite-free and safe Li metal anode.
4.1 Conclusions

Two facile and efficient methods were successfully demonstrated to obtain dendrite-free Li metal anode, by preparing a high modulus and high ionic conductive Li$_3$N artificial layer based on the nitrogen plasma activation and designing a flexible 3D porous copper-clad carbon framework (CuCF) using carbonization and electrodeposition. The as-prepared Li$_3$N artificial SEI layer and 3D CuCF current collector were characterized by SEM, XRD, and Raman spectroscopy. Electrochemical tests were performed to study Li plating and stripping stability. Full cells with modified Li metal as anode and LCO/LFP as cathode were also tested to demonstrate the practical applications of the samples. The main conclusions are as following:

(1) The Li$_3$N artificial SEI prepared by nitrogen plasma treatment was proved to be highly crystalized and oriented in [001] direction, therefore, the Li$_3$N layer was highly ionic conductive (5.02×10$^{-1}$ mS cm$^{-1}$) and mechanically strong (48GPa). Li-ions could easily be diffused through this layer and deposited under the artificial SEI. The dendrites were suppressed due to its high Young’s modulus.

(2) The nitrogen plasma treatment promoted the formation of a dense Li$_3$N layer that is covered the whole surface of the Li metal surface. In comparison, Li$_3$N prepared without plasma showed a lot of creaks. The dense Li$_3$N layer separated the liquid electrolyte from reactive Li metal and reduced side reactions, therefore, decreased the electrolyte depletion.
(3) The optimized Li$_3$N thickness was found to be 8 µm obtained at 2 minutes of plasma treatment time. It showed a stable depositing/stripping cycling stability to 30,000 minutes and high capacity retention of 96% in the full cell after 100 cycles with LCO as the cathode. With a too thick Li$_3$N layer of more than 8 µm, it might hinder the Li-ion transport.

(4) The 3D porous CuCF demonstrated a uniform, dendrite-free Li plating/stripping comparing with CF and planar Cu. It showed a high CE of 99.5% after 300 cycles (~1200 hours) in half cell test and a more than 99% capacity retention in full cell test. It could be attributed to the uniformly distributed Li nucleation sites and reduced local current density.

(5) The as-prepared CuCF has a low mass density. A very high gravimetric capacity of 3001.1 mAh g$^{-1}$ was demonstrated at 16 mAh cm$^{-2}$ which has reached 77.7 % of the theoretical value of Li metal anode (3860 mAh g$^{-1}$). The reason could be attributed to its copper-clad structure which was constructed based on carbon fibers. A thin layer of Cu was coated on its surface by electrodeposition. The low mass density could significantly increase battery energy density.

(6) CuCF showed a flexibility feature that can be folded 100 times without and performance loss. The flexibility enabled an adjustable thickness and could accommodate an extra-large amount of Li. Besides, it provided a possible solution to construct flexible electronic devices in the future.
4.2 Significance

In chapter 2, we have demonstrated that ionic conduction and Young’s modulus are two very important criteria for an artificial SEI layer in Li metal battery. High ionic conductivity enables an easy Li ions transportation while the high Young’s modulus could suppress the dendrite formation. These proposed theories can be used to guide future research to look for other suitable materials as artificial SEI. In addition, we also found that uniform distributed protrusions on the surface might homogenize the distribution of electric field and induce a uniform Li flux, which helps obtain an even Li deposition. This could inspire the research on the Li surface pattern or designing 3D structured current collectors. For the fabrication process, the plasma activation method used in Li3N fabrication has also shown a promising way to reduce the processing time to get a high-quality SEI film. Other high ionic conductive compounds such as Li2S and LiF could be explored using a similar method with a different reactive gas such as H2S and HCF2Cl to generate a plasma atmosphere. The parameters including applied DC power, gas flowrate, and plasma treatment time, of course, still need to be further investigated to get a working artificial SEI.

To fulfill the high energy density requirement of Li metal battery, a light-weight current collector is critically important. We have proposed a 3D current collector with high porosity and uniformly distributed Li nucleation sites in chapter 3. The Li deposition morphology was studied and correlated with the surface and conductivity of the current collector. Due to the non-uniform distribution of conductive spots on the current collector at the carbon-based current collector, the dendrites formed inevitably. Future current collector design should focus on the surface morphology and create uniform nucleation
sites on the 3D current collector to guide the Li deposition. Considering the many materials that have been found to be lithiophilic such as Ag, Sn, and ZnO, these materials can be used as a modification layer onto the current collector either by chemical modification or physical deposition. The conductivity of the current collector is also very important. High conductivity can induce a surface Li deposition while a low conductivity promotes uneven Li nucleation. The method to prepare the CuCF can be borrowed to fabricate light-weight current collectors from other carbon sources. Meanwhile, the electrodeposition method can be applied with other metal coatings such as Ni and Ag.

The research conducted in this dissertation could also be further applied to sodium, potassium, calcium, and other similar metal battery chemistry. Take sodium metal battery as an example, even though it has a much lower specific capacity (1166 mAh g\(^{-1}\)) and lower reduction potential (-2.71 V) than that of Li (3860 mAh g\(^{-1}\) and -3.04V), the sodium source is more abundant than Li. Sodium metal batteries therefore can be a good candidate for large-scale power grid energy storage. To solve the dendrites growth problem in sodium metal batteries, a similar approach can be applied such as creating artificial SEI by plasma treatment or constructing porous current collectors.
4.3 Future work

To make this dissertation more comprehensive, some further work can be done, which might help to get a deeper understanding of Li deposition under different circumstances and push the boundary to future the commercialization of Li metal batteries. Some proposed works are listed below.

(1) The research approaches discussed in Chapter 2 and Chapter 3 can be combined. Specifically, after the pre-deposition of Li into the 3D host, a nitrogen plasma can be applied to obtain a 3D electrode with a Li$_3$N artificial SEI layer. During battery operation, Li ions diffuse through the artificial layer and deposit into the 3D host. Therefore, Li metal can be protected in two ways at the same time. The 3D host lowers the local current collector and the Li$_3$N suppresses the dendrite growth. This might can combine the advantages from both approaches and further boost the battery performance.

(2) Computer simulations such as first principals/density functional theory (DFT) can be used to further understand the battery chemistry. Computer simulations can provide a way to get a much more fundamental understanding of Li transportation through the artificial SEI layer, Li-ion conductivity of different crystal structures and orientations, and the Li deposition behavior on different current collector surfaces. It will be a powerful tool to predict new materials and a new structure for future Li metal battery research.

(3) The chemical composition and crystal structure can be further analyzed by some advanced characterization techniques such as X-Ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). It will help to understand the
growth mechanism of single-crystalline Li$_3$N and the surface chemical bonding information of the electrodeposited Cu. The post-mortem method to study Li morphology has some drawbacks such as Li dendrite structure can be destroyed during the battery disassembling. It is important to investigate Li deposit behavior in a real-time manner. Therefore, in-situ/operando microscopy can also be used to study the real-time Li deposition on the artificial SEI protected Li anode and in a 3D structured current collector.

(4) The cells in this dissertation are tested using a coin cell structure, which is used for foundational study and proof of the concept. In the future, batteries can be fabricated in a pouch cell structure and tested at more strict and practical conditions. To fulfill the commercialization goals, batteries have to use a lean electrolyte condition (less than 3 g Ah$^{-1}$), a limited amount of the Li (less than 3 mAh cm$^{-2}$), and high cathode loading (large than 20 mg cm$^{-2}$). Batteries can be tested in a wide temperature range (-20$^\circ$C – 80$^\circ$C) instead of only at room temperature. Mechanical tests (such as bending and puncture test) can also be done to ensure safe operation under collision conditions.
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CONFERENCE PRESENTATIONS
• **Ke Chen** "SnO$_2$ Nanoparticles Embedded Biochar as Anode Material in Lithium-ion Batteries. " *2019 IEEE International Conference on Electro/Information Technology (EIT)*. Brookings, SD. May 2019

• **Ke Chen** "Plasma Enhanced Formation of Lithium Nitride As Artificial SEI Layer for Lithium Metal Batteries" *The Electrochemical Society (ECS) 235th conference*, Dallas, TX. May 2019.

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