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Chapter

Construction and Modification of Copper Current Collectors for Improved Li Metal Batteries

Shunrui Luo and Kai Pei

Abstract

Metallic Lithium have gained great attention for its high theoretical specific capacity. But continuous growth of Li dendrites upon cycling might cause low coulombic efficiency and serious security issues. Construction of advanced 3D Cu current collectors to regulate Li plating/stripping and improve battery performance is considered as one effective promising strategy. In this chapter, we will discuss the roles and requirements of current collectors in lithium metal batteries. Then methods (dealloying, powder-sintering and 3D printing) employed for construction of 3D Cu current collector and implementation of surface modification (lithiophilic sites and coating layers) will be illustrated. At last, future opportunities of Cu current collectors will be lifted out.

Keywords: Cu current collectors, Li deposition, 3D framework, surface modification, Lithium metal batteries

1. Introduction

With the increasing demand for electric vehicles and portable electronics, there is an urgent need for advanced energy storage systems with high energy density [1]. State-of-the-art lithium-ion batteries (LIBs) with intercalated graphite as anodes and transition metal oxide as cathodes are currently approaching their theoretically energy densities (~300 Wh/kg), which is still insufficient to meet the growing demand of advanced energy storage system and achieve a carbon neutral society [2]. Li metal have gained much attention as anode for its high theoretical specific capacity (3860 mAh g⁻¹), low redox potential (~3.04 V vs. SHE), and low density of 0.59 g cm⁻³, which could boost the energy density of batteries [3]. However, lithium anode has many notorious problems during the cycling process, namely: formation of dendrites, corrosion of lithium, dead lithium, and volume expansion, which will lead to several capacity loss and even explosion of lithium metal batteries [3, 4]. Specifically speaking, the fragile SEI (solid electrolyte interphase) would crack due to huge volume expansion during Li plating (Figure 1, step1), through which Li dendrite will grow (inhomogeneous Li deposition; step 2) [5]. During Li stripping, SEI would be also cracked due to the volume shrink, and ‘dead Li’ (electrically isolated from the substrate) will form from kinks or roots
in a dendrite (step 3). The repeated process will amplify the problem, and finally lead to a porous Li electrode, a thick accumulated SEI layer and excessive dead Li (step 4). The nucleation and growth of lithium dendrites are mainly influenced by types of nucleation [6, 7], distribution of Li ions [8, 9], and charge induction [10]. Until now, various suppression strategies for Li dendrites have been reported, including modification of electrolyte [11, 12], application of different temperatures and pressures [13, 14], fabrication of multifunctional separators [14, 15], etc. Among them, building advanced current collectors are considered an outstanding technique for the suppression of dendritic growth and stable Li anodes in safe Li metal batteries (LMBs) [16, 17].

Current collector is one of the essential components of LMBs, which not only supports anode or cathode materials layers, but also collects electrons from electro-chemical reaction, and bridges with external circuits. The commercially used cathode and anode current collectors for Lithium-ion battery are Aluminum (Al) and copper (Cu) foil respectively. Researched results showed that current collectors have great influence on the resistance and performance of lithium metal batteries [18]. In other words, rate capacity, coulombic efficiency and cycling capacity of LMBs would be enhanced by increasing conductivity, lowering contact resistance, and improving chemical resistance of current collectors. In this chapter, we will introduce the general requirements and challenges for Cu collectors, and strategies employed for construction and modification of copper current collectors for improved Li metal batteries anodes.

2. Copper current collectors

The ideal current collectors for LIBs should involve the following four conditions. (1) High chemical resistance. Current collectors should be chemically stable to active materials and electrolyte during manufacturing and charge/discharge processes. (2) High electrical conductivity. High electrical conductivity of current collectors
allows efficient collecting and transporting of electrons, improved battery performances and alleviated conversion of chemical/electrical energy to heat which would rise the working temperature of LIBs. (3) Lightweight and flexible. Elevated volumetric and gravimetric energy densities could be achieved with lightweight and ultrathin current collectors. Flexible current collectors with elevated mechanical strength could resist the strain and keep their integrity during manufacturing and cycling process. (4) Low-cost and processability. Low-cost and processability of current collectors are very vital for its commercialization.

Copper foil (with a thickness of 5–12 μm) is widely applied as anode current collectors for lithium metal batteries because of its low resistivity (~1.68 * 10^-8 Ω m, 20°C), good electrochemical stability from 0 to 3 V vs. Li/Li⁺ in LiPF₆ electrolyte, low tensile strength (~ 325 Mpa), affordable price ($ 640/m²) and easy access [17]. Until now, Cu current collector structures of Cu foil, Cu mesh and 3D Cu frame works (including Cu foam, coated Cu, and other novel 3D Cu structures) have been reported [17]. The lithiophobicity of Cu usually causes the inhomogeneous distribution of Lithium ions (Li⁺) and the formation and growth of small Lithium dendrites. The small Li dendrites lead to inhomogeneous distribution of the electric field and Li⁺ concentration, which finally promote, under cycling, the growth of dangerous dendritic and mossy Li (Figure 2a) [19]. Li dendrites could penetrate the separator and result in serious capacity decay by a consumption of both Li and electrolyte. This hinders the application of Cu foil and Cu mesh as current collectors. 3D Cu framework with large internal surface area and room could accommodate Li deposition, lowering the electrode current density to suppress/reduce Li dendrite growth and alleviate the huge volume change of Li metal during cycling (Figure 2b) [19]. The presence of lithiophilic sites on the surface of current collectors could decrease the overpotential and result in homogeneous lithium deposition.

In the next section (section3), we will provide a mini-review of some of the methods used for the design and construction of 3D Cu framework as current collectors for Lithium metal batteries. In the Section 4, we will present some of the strategies employed to modify the surface of Cu current collectors and tailor its lithiophobicity.

![Figure 2](image-url)

Figure 2.
A schematic view of the structural changes during Li plating/striping in a conventional 2D planar current collector (a) and a 3D porous current collector (b) (reproduced from ref. [19]).
3. 3D copper frameworks

Alloying/Dealloying is a widely used method for the manufacturing of porous 3D copper current collector by selective “splitting” of metals based on the different chemical, electrochemical and physical properties of the components. Dealloying bimetallic Cu-Zn alloy (brass) [19] in a mixture solution of HCl and NH₄Cl resulted in dissolution of zinc (Zn) and formation of 3D interconnected copper framework. When used as current collectors, the porous Cu skeleton facilitated electron transport and the interconnected pores helped to accommodate the Li deposition. This 3D copper current collector showed excellent performance (97% of Coulombic efficiency for 250 cycles at 0.5 mA cm⁻²) and has commercial potentials in Li-ion batteries. The follow-up works of Yan-bing He et al. [16] showed that a more precisely engraved 3D porous structure could be obtained with electrochemical method by controlling the cycles of electrochemical etching process. The obtained 3D Cu structure with uniform and smooth pores also showed superior mechanical properties and good electrical conductivity. The lithium anode with such 3D Cu current collector achieved stable cycling for 400 h at a high Li plating/stripping capacity of 1 mA h cm⁻² and high current density of 1 mA cm⁻².

Inspired by the fact that lithiophilic metals such as Au, Ag, Mg and Zn presented low nucleation potentials (essentially 0 V) of lithium on them and could promote uniform Li deposition, Jun Lu et al. [20] put forward Cu-Zn alloys (commercially available brass) as lithiophilic materials based on DFT calculations and in situ experiments. Lithiophilic 3D porous Cu-Zn current collector with porous structure and residual CuZn alloy has been prepared by facile chemical dealloying Cu-Zn sheets in hydrochloric acid at various dealloying time (from 0 to 8 h, Figure 3a–h). Li dendrites were more suppressed in 3D porous Cu (8 h-3D Cu) than planar Cu which is consistent with what we discussed above. The 2 h-3D CuZn current collector showed an optimal lithiophilicity with denser and more uniform Li layers (Figure 3i–l), and a high CE (>95% of coulombic efficiency after 220 cycles at 0.5 mA cm⁻²) over 4 h Cu-Zn (97.5% of coulombic efficiency after 135 cycles at 0.5 mA cm⁻²) for elevated Li preferred nucleation sites in the 2 h-3D framework. A painting-alloying-dealloying strategy [21] was developed to fabricate 3D porous Cu by painting melted Ga on Cu foil, alloying at 100°C and chemically dealloying in a solution of nitric acid and hydrofluoric acid. There are also reports on chemical dealloying of alloys like Cu-Al-Mn [22], Al-Cu [23] in solution of HCl and NaOH respectively to prepare 3D porous Cu current collectors. Apart from chemical dealloying method, Cu-Zn alloy can also be dealloyed utilizing a vacuum distillation approach (physical vacuum dealloy) owing to the easily distilled Zn component (bp, 907°C) [24]. As for current collectors based on free-standing copper nanowires network [25], their open porous pores enabled the Li metal to be deposited on the whole surface of the network and fill the pores without dendritic lithium growth.

Powder-sintering is a heat treatment applied to compact powder in order to improve the strength and structure integrity. It is, thought to be a facile, effective, and low-cost way for the preparation of porous materials [26, 27]. The particles of the powder chemically bond to each other and form a consistent shape under a high temperature (below the melting point of the main component). For example, an integrated bidirectional porous Cu (IBP-Cu) film was obtained by powder sintering of commercial Cu powder at a certain temperature range (from 700 to 900°C) [27]. This IBP-Cu film with tunable porosity presented a strong mechanical flexibility and stability. Li/IBP-Cu anode could achieve a capacity of up to 7.0 mAh cm⁻² for deep plating/
stripping and long cycling ability with Coulombic efficiency of $\approx 100\%$ for 1000 cycles at 1.0 mA cm$^{-2}$ and 1.0 mAh cm$^{-2}$. NaCl-assisted powder-sintering (using NaCl as submicron templates) allowed to improve porosity of Cu current collectors and prevent

Figure 3.
(a) Dealloying process schematic diagram (CuZn phases were dealloyed to Cu phases at different time duration). (b–e) SEM cross-sectional and upper surface images of CuZn sheets before and after dealloying at 0, 2, 4, and 8 h. (f–h) EDX cross-sectional images after dealloying at 2, 4, and 8 h. (i–l) Li deposition diagram indicating displaying different current collectors dealloyed with various durations (at 0, 2, 4, and 8 h). (j) Rate performance of different current collectors as Li metal anodes (reproduced from ref. [20]).
congestion of Li-diffusion during Li plating process [28]. As already reported above, 3D Cu skeleton structure [28] with high surface area helped Li homogeneous plating: Li is deposited largely in the internal pores of 3D skeleton rather than outside of the 3D current collectors. Indeed, following the lightning rod theory, the density of charge is higher in areas of high curvature leading to the preferential growth of Lithium inside internal pores [29]. Smooth surfaces facilitate the plating of Li into smooth spherical

Figure 4.
Schematic illustration of the formation of a 3D printed Cu mesh. (a) Preparation of paste. (b) Schematic diagram of the 3D printing mechanism and postprocessing process of the Cu mesh. (c) Mass-produced 3D printed Cu meshes. Morphology of the 3D Cu mesh before (d–e) and after (f–g) heat treatment (reproduced from ref. [37]).
shape, which ease Li dendrite growth. As a result, the 3D current collectors based on NaCl assisted powder-sintering [28] performed a high and stable Coulombic efficiency (higher than 95% for 700 cycles at 0.5 mA cm\(^{-2}\) and 400 cycles at 1 mA cm\(^{-2}\) respectively). Moreover, introduction of lithiophilic components like Zn before powdersintering would enhance the lithiophilicity of the whole current collector [27, 30].

Additive manufacturing (AM, also known as 3D printing) [31] has been employed for the facile and accurate fabrication of 3D architectures by a layer-by-layer depositing phase change materials and solvent-based inks from computer-aided-design (CAD) files. This method has attracted high interests in various areas not limited to the design of 3D architectures as components for energy storage [32–36]. Various 3D print techniques, such as DIW (direct ink writing), IJP (inkjet printing), SLA (stereolithography), FDM (fused deposition modeling), etc., have been employed to manufacture micro-sized components for lithium batteries [31]. For example, a hierarchical 3D Cu current collector [37] was obtained via DIW of copper ink followed with pyrolysis and reduction (Figure 4a). The printing paste was prepared by mixing Cu powder, polyvinylidene fluoride (PVDF), and 1-methyl-2-pyrrolidinone (NMP). High viscosity of the paste can be realized by minimizing the volume of the added NMP, which helps to avoid the collapsing of the extruded lines. A ring electric heater was equipped on the syringe to improve the fluidity of the paste for better extrusion (Figure 4b). The extruded paste was heated on a hot plate to vaporize NMP and induce solidification (Figure 4c). The 3D Cu mesh configuration [37] was finally obtained by heat treatment in air to remove PVDF and then in hydrogen for the reduction of CuO completely to Cu. The large pores of 3D Cu current collector help to store electrolyte and provide spaces for dendrite growth. The small pores generated from the spaces occupied by PVDF (polyvinylidene fluoride) and the space where particles accumulated during heat treatment, would guide dendrite deposition. Thus, the Cu current collector-based anode showed enhanced deposition and stripping capability (50 mAh cm\(^{-2}\)), high-rate capability (50 mA cm\(^{-2}\)), and a long-term stable cycling (1000 h). The 3D printing ink formula and printing process can be guided by machine learning [38]. In another example, a 3D-printed Cu (3DP-Cu) was fabricated by extrusion DIW approach with a mixture of copper particles, Pluronic F127 (PF127) and water used as printing ink [39]. The 3DP-Cu exhibited good mechanical stability and robustness even under a high pressure of around 1.4 MPa.

4. Surface modification

Apart from constructing 3D current collectors to attain uniform striping and plating of lithium, smart surface modification of copper-based current collectors to enhance lithiophilicity and lower interfacial energy between lithium and the substrate could also favor uniform deposition of Lithium. Next, we will mainly discuss some of the strategies employed for the surface modification of Cu-based current collectors.

4.1 Introducing lithiophilic sites

Lithiophobicity of Cu constrains its application as current collector for Li Metal based batteries due to high deposition overpotential of lithium. Introduction of lithiophilic sites could decrease the overpotential and result in smooth lithium deposition. Lithium nucleation overpotential of a list of 11 elements (Au, Ag, Zn, Mg, Al, Pt, Si, Sn, C, Cu, and Ni) substrate materials were carefully studied by vacuum deposition
of these materials (with a thickness of 50 nm) on Cu foil as working electrode. The related voltage profiles are shown in Figure 5(a and b) [40]. Voltage profile of Cu shows a major voltage dip and a followed flat voltage plateau (10 μA cm$^{-2}$) (Figure 5(b) red line), while Au, Ag, Zn and Mg showed zero overpotential during deposition of Li. When Cu substrate patterned with Au stripes was used for galvanostatic deposition, Li was found on the surface of Au strips, whereas no Li were found on the bare Cu surface (Figure 5c). C, Sn and Si showed a lower Li nucleation overpotential compared with Ni and Cu. In addition, the element Sb [41], other metal compounds (like Cu$_2$O [42], CoO [43], etc.) and polymers (like polydopamine, etc.) were also shown to have a low overpotential and trigger an uniform Li deposition when coated onto Cu current collectors. These materials are usually applied as a coating layer on the current collectors and will be discussed in the next section.

4.2 Create a coating layer

The coating of Cu current collectors with various materials offers substantial benefits. Carbonaceous materials have been widely used for the fabrication of core-shell structured composites and also applied in energy storage for their high conductivity, lightweight, and good chemical stability, etc. 3D Cu foams wrapped with N-doped porous carbon nanosheets (with a thickness from several to 35 nm, NPCN) were obtained by dip-coating process [44]. The lithiophilicity and large surface area of such NPCN could help to regulate Li deposition and avoid Li dendrites even at a high Li deposition capacity of 10 mAh cm$^{-2}$. The Li/Cu@NPCN||Li cell demonstrated a high coulombic efficiency and a low hysteresis after cycling for 1600 h (0.5 mA cm$^{-2}$). Graphene film modified Cu foam doped with Br- and CuBr- (BGCF) could guide Li$^+$ flux and therefore achieve an homogeneous Li deposition [45]. Also, CuBr are able to react with Li to form LiBr which offers a fast Li diffusion pathway. Pancake-like Li seeds and further Li metal were observed under a current density of 2 mA cm$^{-2}$. Li||Li-BGCF symmetrical cell attained a cycling stability of 850 h (1 mA cm$^{-2}$, Figure 6c). Li||LiFePO$_4$ full batteries fabricated with those BGCF maintained 94% of their initial capacity after 400 cycles with a cathode loading of 2 mAh cm$^{-2}$. Besides, porous carbon nanosheets, carbon-based materials like graphene [47], carbon nanofibers [48] wrapped Cu current collectors have been reported to regulate Li deposition and alleviate Li dendrites. The addition of carbon-based materials improves chemical stability and charge transfer kinetics. Note that the thickness of carbon coating layer should be precisely controlled and parameters like porosity, surface treatment, etc. should be investigated for a further understanding of the mechanism.

The growth of vertically aligned CuO nanosheets on planar Cu (VA-CuO NSs) were realized by immersing Cu foil in NH$_4$OH solution [42]. The intimate contact between CuO nanosheets and Cu foil ensures the good conductivity of the electrode. The CuO nanosheets enabled increased affinity with Li, which ensures uniform Li nucleation. When exploited as current collectors, the Li||VA-CuO-Cu preserved 94% of the coulombic efficiency after 180 cycles (1 mA cm$^{-2}$). A Cu foils with Cu pillar arrays were fabricated by templated electrodeposition with controllable pillars diameters and pore spacing (Figure 6d and e) [46]. This vertical pillar architecture could block Li$^+$ flux on the top of pillars and result in Li deposited within the pores rather than on the top of the pillars arrays, which reduced safety issues. When coated with a thin layer (50 nm) of ZnO by atomic layer deposition (ALD), this core-shell pillar architecture facilitated uniform Li deposition. With synergistic effect of ALD surface modification, the cycling lifetime were tripled (>180 h) [46]. Until now, Sb
When a thin β-PVDF (Poly(vinylidene difluoride)) layer with high dielectric constant (8–13) was coated on copper foil, the formed β-PVDF@Cu attained dendrite-free Li deposition up to 5 mA cm$^{-2}$ and enhanced battery performance for Li metal anodes [49]. Firstly, the polarity of PVDF redistributed Li-ion flux through the interactions between Li ions and its polar groups. Secondly, the alignment of F atoms facilitated uniform Li deposition for interaction between the electronegative C-F groups and Li at the interface. Also, F atoms on the PVDF induce preferential Li diffusion path and allow to achieve high-rate Li plating/stripping. For polydopamine (PDA) modified Cu foil [50], PDA reacts with Li via the carbonyl groups complexing with Li. This uniform distribution of Li ions helps to achieve uniform Li deposition on the surface of current collector. In addition, conductive polymers like poly(dimethysiloxane) (PDMS) [51], poly(3,4-ethylenedioxythiophene (PEDOT) [52], polyaniline (PANI) [52], etc. have been reported for the modification of Cu foil as improved current collectors. Conductive polymers are potential candidates for current collectors thanks to their low densities, good mechanical strength, and chemical resistance. Nevertheless, the conductivity and thermal stability need be improved to meet commercial requirements.
5. Conclusion

The Li metal battery technology has attracted great attentions for their high energy capacities and low density. However, poor chemical stability, growth of Li dendrites, and unstable electrode-electrolyte interfaces hinder its utilization. One of the effective strategies is the development of advanced current collectors to regulate Li plating/stripping and improve performances. 3D Copper current collectors with a large surface area could lower local current density and constrain volume changes, which would effectively prevent lithium dendrites growth and mitigate volume
changes. The methods of dealloying, powder-sintering and 3D printing have been discussed for the realization of 3D Cu frameworks. Surface modification strategies mainly includes introduction of lithiophilic sites through coating layers (metal composites, carbon-based materials and polymers) to regulate Li ion deposition and avoid Li dendrites. Thus, stable coulombic efficiencies and prolonged cycling lives were achieved. As shown in this chapter, the development of advanced Cu current collectors to fabricate high gravimetric/volumetric energy densities Li metal batteries with long cycling life will have to consider all the parameters, like porosities, thickness, morphologies, cost, feasibility, etc., and utilize not only one strategy for their construction. For future current collectors, the mechanism governing Li dendritic growth will also need more in-depth investigation, more precise preparation control to promote their actual application and achieve mass production.

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