Lithiophilic coating layer modify three-dimensional Cu foam for stable and dendrite-free lithium metal anode

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Abstract. The widespread research for lithium metal anodes (LMA) has been rapidly developed in recent years. However, undesirable dendritic structures generated in the process of unstable lithium (Li) deposition dramatically restricts the cycle life of LMA. The skeleton structure of the three-dimensional (3D) host substrates are the potential promising host for Li, which can alleviate volume expansion during cycling. Herein, we propose a facile surface modification approach through ion sputtering, which can effectively regulate the lithiophilic properties of Cu foam (CF) for facilitating Li deposition. Au modified surface can enhance the lithiophilic property of substrates and induce uniform Li deposition along the conductive skeleton. Further analysis of results, substrate with Au coating modified surface exhibits a smaller Li nucleation overpotential (12 mV), a more stable coulombic efficiency (CE) at different current densities, and more uniform morphology of Li deposition with dendrite-free at large capacity of 4 mAh cm⁻². Meanwhile, symmetric cells with Au coating on CF can stably operate more lifespan than other samples. Furthermore, full cells paired with LiFePO₄ cathodes and CF coated Au exhibit remarkable discharge capacities and capacity retention than others. This work provides new insights toward developing excellent 3D skeleton with modified surface for dendrite-free LMA.

1. Introduction
Lithium metal is an ideal anode to carry out the high energy density in next generation energy storage devices with the high theoretical capacity (3860 mA h g⁻¹) and the lowest electrochemical reduction potential (-3.04V) [1,2]. However, the safe commercial application of Li anode has been severely limited because of uncontrollable metal dendritic growth during Li plating/stripping processes, which leads to serious deterioration in CE and cycling performance [3]. Moreover, the further formation of Li dendrite is often accompanied by short circuit for batteries, thus causing some security risks. [4].

Recently, significant efforts have been proposed to solve these issues in Li metal anode. Surface modification for Li anode is a commonly used method to mitigate the tendency of dendrite growth. For example, electrolyte additives have been applied to promote the formation of relatively stable solid electrolyte interphase (SEI) [5,6]. Besides, coating technologies can also be used to form artificial surface on Li metal to construct a durable SEI during the short-term cycle [7,8]. Although these methods slow down the dendritic Li growth, it is still a challenge to achieve high CE and long-cycling life for Li metal batteries with dendrite-free plating/stripping of Li at both high current densities and high deposition capacities.

Inspired by the Sand’s time, utilizing 3D skeleton structure is an available way to restrain Li dendrite growth through cutting down local current density [9,10]. Furthermore, 3D substrates with electronic conductivity could provide excellent charge transfer kinetics, and avoid the huge volume changes during
deposition process by 3D storage space for lithium. Based on the benefits mentioned above, a multitude of 3D skeleton structures have been researched, such as porous carbon fibers [11], metal foam [12-14] and graphene networks [15]. These 3D structures have large specific surface area and space structure, which could effectively regulate Li deposition and restrain volume changes during cycling. Commercial CF with remarkable structure stability, excellent electrical conductivity and low cost has been employed as 3D skeleton substrates for Li deposition [16]. However, the direct utilization of CF as the current collector for Li deposition could lead to uncontrollable Li dendrite formation and drastic reduction in CE, which may owe to the intrinsic lithiophobicity of the CF surface.

Herein, we propose a simple and convenient method to modify surface properties of 3D CF by sputtering Au or Ag coating layer on the skeleton surface, which could enhance surface wettability of 3D substrates through lithiophilic property and form Li-Ag or Li-Au alloy layer during initial activation process to stabilize Li deposition. And we systematically studied the relationship between surface wettability and surface coating layer of the 3D CF. The modified surface layer can effectively reduce the Li deposition overpotential of 3D substrate, which guaranteed uniform Li deposition and retarded dendrite formation. As a result, the 3D surface modified CF substrates were demonstrated as an ideal anode skeleton for inhibiting Li dendrite and mitigating volume change during cycling, which maintained high CE and prolong cycle life during stripping/plating processes. Besides, LiFePO₄ (LFP)||Li full cells showed excellent capacity retention. Furthermore, Au coating 3D CF sample had better electrochemical properties than Ag coating sample, so Au coating is a better surface modification layer for promising LMA with preeminent cycling performance.

2. Materials and methods

2.1. The preparation of 3D skeleton with modified surface

A piece of CF was first cut into 1 cm disks and washed by acetone, alcohol and deionized water for three times to remove surface impurities (thickness 500 µm, purity 99.9%). Thin coating layer of Ag and Au with a thickness of 50 nm were directly deposited onto CF by small ion sputtering instrument (SBC-12) to get Ag coating-Cu foam (Ag@CF), and Au coating-Cu foam (Au@CF). The sputtering time was 10 minutes and the layer thickness was 50 nm approximately.

2.2. Battery assembling and electrochemical test

For Li||CF coin cells, 60 µl electrolyte of 1 M LiTFSI in DOL/DME (1:1 by volume) with 1 wt% LiNO₃ additives. The cells were first cycled at 0.01-1.0 V (vs Li/Li⁺) at 0.05 mA for 5 cycles to stabilize the SEI. In each galvanostatic cycle, a fixed amount of Li (1 and 2 mAh cm⁻²) was deposited on the CF and stripped away up to 1 V. The symmetric cell was also composed of Li||CF structure with 60 µl same electrolyte, which firstly cycled at 0.05 mA between 0.01-1 V for 5 cycles. Then, 2 mA cm⁻² Li was plated on the foam structures at 0.5 mA cm⁻², following the repeated Li striping/plating at 0.5 mA cm⁻² for 1 h or 3.0 mA cm⁻² for 10 minutes in each cycle. The electrochemical impedance spectroscopy was tested on Princeton VersaSTAT 3F electrochemical workstation with an amplitude of 10 mV over a frequency range from 100 kHz to 0.1 Hz. For the full cells, LFP was employed as cathode material casted on an Al foil. Li/CF, Li/Ag@CF, and Li/Au@CF anodes were obtained from preprocessed half cells with 50 µL 1 M LiPF₆ in EC/DEC as the electrolyte. After depositing 2 mAh cm⁻² of Li onto the foam collectors, the anodes were extracted from the half cells and reassembled into full cells against LFP cathode operated in a voltage window of 2.2-4.0 V with same electrolyte.

2.3. Characterizations

The morphology and structural characteristics of foam structures were investigated by field-emission scanning electron microscope (SEM, S4800). For ex-situ characterization of Li deposition morphology on 3D foam, cycled cells were disassembled in glove box and washed with DME to obtain Li deposited anodes.
3. Results & Discussion

3.1. Wettability of different 3D skeleton for molten lithium

Firstly, to study the wettability of different substrates for molten Li, confirmatory experiment consists of sputtering and thermal infusion processes as presented in Figure 1a. The lithiophilicity of CF, Ag@CF, and Au@CF collectors were investigated preliminarily by molten Li in Figure 1b-1g. It was clear that Ag@CF and Au@CF samples presented much better wettability with molten Li uniformly spread out on the 3D substrates in comparison with CF sample. Moreover, molten Li appeared as a droplet shape on the surface of CF substrate. These optical photographs directly demonstrated that the modified coating layer with Ag or Au would change CF collector from lithiophobic to lithiophilic.

3.2. Electrochemical performance and morphology of different 3D skeleton

Before investigating the CE of different 3D substrate collectors, the nucleation overpotential of the metallic Li deposition on CF, Ag@CF, and Au@CF collectors were researched by the difference value between sharp tip voltage and later stable voltage for evaluating their lithiophilicity. As shown in Figure 2a, at 0.5 mA cm⁻², the nucleation overpotential of Li deposition on CF, Ag@CF, and Au@CF collectors were 31, 15, and 12 mV, respectively. This result indicated that the excellent lithiophilic property of Ag and Au coating on 3D collectors, which agreed with the previous report that lithiophilic surface had better wettability and thus allowed uniform Li nucleation. However, pure CF has little solubility in Li metal to prevent the formation of alloying phases during Li deposition, resulting in large nucleation overpotential. In addition, during the initial activation process (galvanostatic discharge/charge between 0.01 and 1 V for 5 cycles, Figure 2b), the Ag or Au coating layer on CF would form uniform alloying phases on the CF surface as homogeneously protective layer. This high conductivity protective layer could effectively avoid the directly continuous contact of Cu substrate and metallic Li with the electrolyte during deposition process, which suppressed excessive Li deposition at the localized area with broken surface layer.
Figure 2 (a) Nucleation overpotential of Li on different 3D substrate collectors. (b) Galvanostatic discharge/charge profiles of different 3D foam electrodes between 0.01 and 1.0 V for 5 cycles. CE of different 3D substrates, (c) 1 mAh cm\(^{-2}\) at 1 mA cm\(^{-2}\), (d) 2 mAh cm\(^{-2}\) at 2 mA cm\(^{-2}\).

CE is defined as the ratio of stripping Li capacity to Li deposition capacity at every cycle during the discharge/charge process, which is usually used to evaluate the electrochemical performance of different electrode. Different amounts of Li were deposited on different collectors at different current densities. As shown in Figure 2c, with a cycling capacity of 1 mAh cm\(^{-2}\) at 1 mA cm\(^{-2}\), high average CE of 95\% after 200 cycles could be obtained for Ag@CF and Au@CF collectors. In comparison, the CE of CF collector could remain relatively stable for 100 cycles, but began to decay rapidly at 120th cycle and dropped to below 80\% after another 10 cycles. Further increasing the cycling capacity to 2 mAh cm\(^{-2}\) at the current density of 2 mA cm\(^{-2}\), a stable 80 cycles can still be achieved with high average CE of 95\% for Au@CF collectors (Figure 2d), while the CE performances of Ag@CF was fluctuant and dropped down after 60 cycles. Meanwhile, CF collector began to decay after 40 cycles. These results were attributed to the excellent lithiophilic property of Ag@CF and Au@CF collectors, which could reduce the nucleation overpotential and remove the deposition barrier during the discharge/charge process. Moreover, the Au@CF collector showed better CE performance at higher current density.

Symmetric cells were also prepared to evaluate the long-term stability by galvanostatic Li plating/stripping.
Figure 3 The voltage-time curves of CF, Ag@CF and Au@CF samples in symmetric cell test. (a) 0.5 mA cm$^{-2}$ for 1 h. (b) 3.0 mA cm$^{-2}$ for 10 minutes. (c) The Nyquist curves of the CF, Ag@CF and Au@CF samples after plating 1 mAh cm$^{-2}$ Li at 1 mA cm$^{-2}$.

cycling test. Prior to the test, 2 mA h cm$^{-2}$ Li was plated on the foam structures at 0.5 mA cm$^{-2}$. As shown in Figure 3a, with the capacity of 0.5 mAh cm$^{-2}$, the cell assembled with Au@CF presented a stable Li plating/stripping voltage curve over 350 h at a current density of 0.5 mA cm$^{-2}$. Meanwhile, in the Ag@CF sample, the platform voltage had the gradual increase, which could be observed within 300 h. In comparison, a sharp increase in the voltage of the cells with CF collector could be observed after only 150 h. Even at increscent current density (3 mA cm$^{-2}$), the Au@CF sample still exhibited much lower and more stable voltage-time curve (Figure 3b), revealing its conspicuous advantage of repeated Li plating and stripping. However, the Ag@CF and CF samples began voltage enhancement around 40 and 20 h, respectively. As shown in Figure 3c, the results were consistent with the lowest charge transfer resistance of the Au@CF among the samples, further indicating that there was superior interface performance of the Au@CF.

Figure 4 Morphology characterizations of Li deposition on different 3D substrates after plating 4 mAh cm$^{-2}$ at 1 mA cm$^{-2}$. (a, b) CF, (c, d) Ag@CF, (e, f) Au@CF.
In order to research the morphology characteristics of Li deposition on different substrates, Li was deposited on these substrates at 1 mA cm\(^{-2}\) with capacity of 4 mAh cm\(^{-2}\), and the results are shown in Figure 4. After depositing 4 mAh cm\(^{-2}\) of Li, a large number of mossy and undulating Li deposits were scattered on the skeleton of CF, which could lead to the Li accumulation and dendritic Li formation (Figure 4a,4b). On the contrary, due to the lithiophilic protective layer promoting the Li plating, Ag@CF and Au@CF samples had no obvious mossy morphology on the surface (Figure 4c,4e). To further comparison, from the corresponding high magnification SEM image (Figure 4d,4f), metallic Li was uniformly deposited into the interior space and the surface of the 3D Au@CF skeleton without any Li dendrite. While, on the other hand, metallic Li was not sufficient smoothly to cover the Ag@CF skeleton surface, and some mossy Li was also appeared on the surface under high magnification conditions.

3.3. Application in full cells

Figure 5 Electrochemical performances of full cells with different 3D structure anodes. (a) cycling performances at 1 C (1 C = 170 mAh/g) and (b) rate performances of Li/CF||LFP, Li/Ag@CF||LFP, and Li/Au@CF||LFP.

To further evaluate the practicality of different 3D structures, 2 mAh cm\(^{-2}\) Li plated on 3D foam structures were used as the anode in full cells paired with LFP cathodes. As shown in Fig. 5a and 5b, compared with Li/CF||LFP, Li/Ag@CF||LFP, and Li/Au@CF||LFP, the full cell using the Li/Au@CF anode exhibited an excellent cycling stability (126 mAh g\(^{-1}\) at 1 C after 160 cycles). In comparison, cell with Li/CF anode began to decay rapidly about 15th cycle. And Li/Ag@CF anode also began to decay after 150 cycles. Besides, both Li/Ag@CF and Li/Au@CF anodes had good rate capability from 0.5 C to 5 C, and the rate capability of Au@CF sample was a little bit bigger than Ag@CF. This excellent electrochemical performance of Au@CF sample could be also attributed to the stable dendrite-free surface of Li-Au alloy during cycling.

4. Conclusion

In summary, we develop an available method to modify the surface of 3D CF substrate with the Ag or Au nanoparticles by the simple ion sputtering. The good lithiophilic property of Ag or Au coating layer can not only reduce the nucleation barrier but also guide the uniform lithium nucleation with uniform deposition morphology and dendrite-free. Moreover, Au@CF sample showed better electrochemical performance with more uniform deposition topography, which could cycle stably with high average CE of 95% over 200 laps at 1 mA cm\(^{-2}\) and 80 laps at 2 mA cm\(^{-2}\). Besides, a prolonged cycle stability close to 350 h at 0.5 mA cm\(^{-2}\) and 60 h at 3 mA cm\(^{-2}\) were obtained in symmetric cells, respectively. In addition, the assembled Li/Au@CF||LFP full cell exhibited a much higher capacity retention than other two substrates after 150 cycles. These superiorities prove a facile method to construct excellent 3D substrates for Li deposition and provide a valuable strategy to promote the development of LMA.
Acknowledgments
This work is supported by the National Key Research and Development Program of China (2017YFB0702802).

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