Lithium Metal Anodes



A Versatile Strategy to Fabricate 3D Conductive Frameworks for Lithium Metal Anodes

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The suppression of lithium dendrite is critical to the realization of lithium metal batteries. 3D conductive framework, among different approaches, has shown very promising results in dendrite suppression. A novel cost-effective and versatile dip-coating method is presented here to make 3D conductive framework. Various substrates with different geometries are coated successfully with copper, including electrically insulating glass fiber (GF) or rice paper and conducting Ni foam. In particular, the as-prepared copper coated GF shows promising results to serve as the lithium metal substrate by the electrochemical battery tests. The method significantly broadens the candidate materials database for 3D conductive framework to include all kinds of intrinsically insulating 3D substrates.

1. Introduction

Developing advanced electrode materials is critical for highenergy-density rechargeable batteries. Lithium metal with its extremely high specific capacity (3860 mA h g⁻¹) and the lowest redox potential (-3.04 V vs the standard hydrogen electrode) has been long regarded as an ideal anode material. However, the dendrite problem has largely limited its commercialization.^[1] Uncontrolled dendrite growth can penetrate the separator, causing short circuits and even catastrophic explosions.^[4] Lithium dendrites were thought to originate from the inhomogeneity of the Li⁺ concentration on the traditional anode surfaces and the drastic electrode dimensional change during cycling.^[2]

Various strategies have been proposed to suppress the dendrite growth. Many approaches focus on improving the stability and uniformity of the solid electrolyte interphase (SEI) layer by optimizing electrolyte components including adding Cs+ and Rb⁺,^[3] LiF,^[4] vinylene carbonate (VC),^[5] or Li₂S₈.^[6] However, due to the "hostless" nature of Li metal with volume expansion toward the separator,^[7] cracking SEI layers upon cycling can expose the fresh Li metal upon further reaction. Solid or polymer electrolytes are promising to suppress the lithium dendrite growth if the issues of lithium penetration through the cracks or grain boundaries of the solid electrolyte can be solved, together with some other issues such as lower ionic conductivity or interface reaction of solid and polymer electrolytes.^[8]

As an alternative, ex situ coated artificial SEI layers such as polydimethylsiloxane (PDMS),^[9] boron/graphene,^[10] or silica layer^[11] present efficient interfacial protection.

Recently, various novel "host" designs have demonstrated their power in changing the Li plating behavior. Conductive micro-/ nanostructure frameworks have proved to be an effective method to ensure uniform Li deposition and to accommodate the Li volumetric expansion^[8g]; these frameworks include the layered reduced graphene oxides,^[2b,12] nickel (Ni) foam,^[13] and metal-coated sponges.^[14] However, the expensive and complex fabrication process may limit practical applications. Developing a simple, lowcost, and versatile technique that can transform materials into 3D conductive frameworks remains a challenge in this field.

In this work, we demonstrate a novel strategy that can implement such a transformation at large scale.^[15] Through two simple

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dip-coating steps, we realize adhesive and uniform copper coatings on various common substrates to build 3D conductive current collectors. Unlike many other approaches, this dip-coating method requires no special chemicals, equipment, or facilities and proves to be an extremely versatile platform to construct a 3D Li host scaffold on virtually all types of materials ranging from metal foams, everyday objects (rice paper), inorganic oxides (glass fiber) to organic polymers (polyether, polycarbonate). For example, the nonconductive glass fiber (GF), which is widely used as separators in sodium ion batteries, is transformed by this method into 3D copper current collector (GF-Cu). We also demonstrate that Li dendrites are well controlled via manipulating Li⁺ flux homogeneity through GF-Cu conductive networks, giving rise to a uniform Li nucleation and growth. Moreover, the original structure of GF was well retained in GF-Cu, which provides the space for volumetric expansion of lithium metal. Therefore, the Li metal anode with such a 3D porous current collector of GF-Cu shows a stable Coulombic efficiency (CE) of \approx 94% over 600 h at 0.5 mA cm⁻² in a conventional carbonate electrolyte. In addition, when coupled with the LiFePO₄ cathode, the full cell exhibited an improved cycling stability up to 200 cycles. This simple yet versatile method will serve as a very powerful tool to change many otherwise impossibleto-use substrates into 3D conductive matrices as candidates for lithium metal anodes. It will hence open up a new design principle for 3D scaffold conductive structures and will significantly broaden the candidate database for the lithium metal anode for next-generation lithium ion battery applications.

2. Results and Discussion

The procedure to obtain the 3D porous Cu foil is schematically presented in Figure 1 and illustrated using different original



materials in Figure 2a. The preparation process first involved the immersion of the substrates in an aqueous dopamine solution and then dipping polydopamine (PDA) coated objects into CuCl₂ solutions. After the first immersion step of 24 h the colors of all the samples, including a metal coin, polyester, polycarbonate, paper, GF, and nickel foam, changed toward brown, which clearly demonstrated that an adherent polymer film was deposited on the object surface (Figure 2a). Further evidence for dopamine polymerization was found by X-ray photoelectron spectroscopy (XPS) measurements. Taking the GF as an example, the characteristic XPS substrate signals for unmodified GF, such as silicon (\approx 100 eV), were highly suppressed after PDA coating. Instead, nitrogen (≈399.5 eV) in PDA was clearly observed, as shown in Figure 2b. Scanning electron microscopy (SEM) images showed that before and after coating with PDA, the pore-size distributions were almost identical, as shown in Figure 2c,d; this suggested that the PDA coating has little influence on the pore-size distributions of the substrates. The preserved porous nature was confirmed by quantitative analysis of the porosity measurement. As shown in Figure S2 (Supporting Information), the PDA coating does no harm to the porosity of the substrates for the specific battery application of interest here.

After the PDA coating, the metal-binding ability of catechols was exploited to form homogenous metal coatings via a one dip-coating step. The distinct color transformation after the Cu coating step for all the samples in Figure 2a demonstrated the high efficiency and generality of our method, which can coat Cu onto any original material, from metal to insulator, and with all kinds of microstructures (Figure S3, Supporting Information). Furthermore, the procedure only involves low-cost compounds and operations under mild reaction conditions. Similar to the PDA coating, XPS results (Figure 2b) confirmed the success of the metal film deposition and the porosity measurements (Figure S2, Supporting Information) showed no significant



Figure 1. Schematics of converting porous structure into conductive 3D current collector. a–b) Immersion of the GF in the dopamine solution with the color change from white to brown. b–c) Through simple dip-coating operation PDA coated GF turned into Cu coated 3D conductive frameworks. The enlarged image in (c) illustrated the adherent PDA and Cu film on the original structure.







Figure 2. Characterization of dip-coating-treated GF frameworks. a) Digital camera images of original samples (upper), PDA coated ones (middle), and Cu coated ones (bottom). Six different substrates from left to right are metal coin, polyester, polycarbonate, rice paper, GF, and nickel foam. b) XPS spectra of GF, PDA-coated GF, and Cu-coated GF. c–e) Pore size distribution of pristine, PDA-coated GF, and Cu-coated GFs in SEM images.

reduction of the pore sizes. In addition, similar results in the porosity (Figure S2, Supporting Information) and XPS signals (Figure S4, Supporting Information) of the other substrate of polycarbonate confirmed that the effectiveness of this procedure was not limited to GF, but is rather general. Therefore, via this simple and low-cost "dipping-coating" method, common porous frameworks can be easily turned into a conductive 3D matrix ready for further Li deposition with conformal Li entrapment for lithium anode applications.

The stabilization of the electrode dimension is highly beneficial in lithium metal anodes. When deposited on a 2D planar substrate, small dendritic Li grows from bare planar electrodes to promote further dendrite growth. Also, drastic volume expansion during continuous cycling can easily destroy the SEI layer, which in turn results in the inhomogeneous concentration of Li+ flux to further accelerate the Li dendrite growth and the rapid consumption of the electrolyte. In contrast, the design of the 3D conductive frameworks with large internal surface area can effectively reduce the current density and provide enough space to accommodate the Li deposition and alleviate the huge volume change of Li metal during battery cycling. Moreover, the interconnecting conductive inner-structure can effectively regulate the electronic and ionic transportation and distribution properties. As shown in Figures S5 and S6 (Supporting Information), distinct "hot spot" regions with high local current densities are observed among the top regions of Li metal nuclei. These unconstrained hot spots will eventually grow into the Li dendrites. In contrast, the hot spots are effectively prevented with the introduction of the 3D conductive structure due to more homogeneous distribution of the electric fields. Hence the more uniform Li deposition should improve the lifespan of Li-metal anodes.

To confirm this hypothesis, the planar copper and the 3D conductive frameworks based on five different materials are used here as the counter electrodes, respectively, to observe the anode morphologies. In this work, standard carbonate electrolyte (1 м LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC)) was used without other additives. Compared with either electrolyte, it shows more intrinsic improvement related to the 3D structure, since the SEI layers formed are dominated by Li alkyl carbonate (ROCO₂Li) in carbonate electrolyte and are usually too fragile to prevent the Li dendrite formation.^[16] First, 1.0 mA h cm⁻² lithium was first deposited on planar copper and 3D conductive frameworks at 0.5 mA cm⁻² and the stripping process was cut-off at 0.5 V. SEM images clearly demonstrated the lithium morphology after 20 and 100 cycles (Figure 3). The current density in Figure 3 is 0.5 mA cm⁻²; at such a low current density, small Li particles grow from both bare planar and 3D electrodes. However, upon cycling lithium particles are hosted well by the Cu wire in the 3D structure, while lithium metal chunks were formed on the 2D copper foil. For 2D planar copper anodes, there was a large area of bumpy Li plated on the Cu surface as demonstrated in the Figure 3c after 20 cycles. As the cycling time increases, electrons tend to accumulate at the sharp ends and drastically amplify the growth of lithium dendrites, consuming







Figure 3. SEM images of the morphology of Li deposited on 2D and 3D current collectors with current density of 0.5 mA cm⁻² for a total of 1 mAh cm⁻² of Li. Top view SEM images of the a) 20th Li plating, and c) 100th Li plating on pristine 2D planar current collector. Top view SEM images of the 3D porous current collector at b) 20th Li plating and d) 100th Li plating. The schematics of lithium plating on e) 2D copper and f) 3D framework.

much electrolyte, and further resulting in inhomogeneous Li deposition.^[17] On the contrary, the fully plated Li morphology on the 3D copper current collectors differs significantly from that on the planar Cu. Taking the 3D GF-Cu as an example, the surface after 20 cycles remained flat with no obvious Li dendrites from SEM. Upon further plating, micron-sized Li particles gradually deposited in the porous structure and grew into lumps instead of dendritic or mossy morphology. This effective accommodation of lithium is due to the high specific surface area of the 3D conductive structures, where the active surface area for lithium plating is much higher than ordinary planar Cu. Consequently, the actual local current density is significantly reduced in the 3D anode, consistent with our simulation as shown in Figures S5 and S6 (Supporting Information). In addition, we also investigated the morphology change of the 3D porous current collector after Li stripping. As shown in Figure S7

(Supporting Information), the integrity of these porous structures can be preserved well when the deposited Li strips out of the composites, indicating good mechanical properties.

CE is a critical parameter to evaluate the cycling sustainability of Li. Thus two-electrode cells (3D GF-Cu/Li and planar Cu foil/ Li) were assembled to investigate the overall electrochemical performance. As expected, the 3D GF-Cu current collector presented a more stable and longer cycling life. The electrode current density was first set as 0.5 mA cm⁻² for a constant charge capacity of 1 mA h cm⁻². The CE of 3D GF-Cu could maintain an average value of 94% for more than 200 cycles (**Figure 4**a), while that of the control Cu foil exhibited a continuous degradation during the cycles, indicating the unique advantages of the 3D GF-Cu with a larger reversible capacity and reusable Li. In the initial several cycles, the relatively low CE resulted from the electrode activation and formation progress of a stable SEI layer.





Figure 4. Comparison of CE of Li deposition on 2D planar and 3D porous current collectors Li deposition/stripping at various current rates of a) 0.5, b) 1.0, and c) 2.0 mA cm⁻² with the same areal capacities of 1 mA h cm⁻².

The initial plated Li on the 3D framework has a high surface area and it tends to react with electrolyte more than the plated Li on the 2D Cu foil. After first several cycles, the CE of planar Cu electrode is lower than 3D GF-Cu, which may be related to the formation of dendritic lithium metal and the cracking of SEI. At a high current density of 1.0 and 2.0 mA cm⁻² that usually results in low efficiency and rapid dendrite growth, the differences between two samples are even more obvious (Figure 4b,c). SEM images of the Li deposited 2D and 3D current collectors at a high current density are shown in Figure S8 (Supporting Information). The extremely inhomogeneous lithium deposition can be obviously observed on the 2D Cu foil, while the surface of 3D GF-Cu is even. The 3D GF-Cu presented superior cycling performance for more than 100 cycles at 2 mA cm⁻², while the planar Cu foil current collector exhibited much larger fluctuations in CEs and an obvious drop at 50 h (Figure 4c). Previous studies^[12b,18] have shown that high current rates not only generate more dendrite growth, but also can cause more severe damage to the SEI layer.^[11,19] The stable cycling of the modified cells at relatively high current density hence indicates that the free-standing 3D GF-Cu membrane is effective in suppressing Li dendrite growth.

The voltage profiles of Li-plating-stripping process were also investigated for all the samples. The voltage hysteresis is defined as the difference between the voltages of lithiation and delithiation performances, which is mainly influenced by the current density and interfacial properties. Figure 5a shows the stable deposition/stripping behaviors of 3D GF-Cu with the nearly constant hysteresis of 40 mV. The reduced polarization of Li plating/stripping on the 3D GF-Cu is generally stable without obvious fluctuations for 150 cycles, while for 2D Cu foil-based anode, the hysteresis of Li depositing/stripping was much larger (≈70 mV) in Figure 5b. The difference of the voltage hysteresis for the 2D and 3D copper foils is summarized in Figure 5c. The large irreversible deposition may induce thick and unstable SEI layers, consume more Li and electrolytes, cause the capacity loss and further lead to short circuits.^[20] As evidenced in Figure 3, large masses of visible dendrites and dead Li were found on the surface of bare Cu foil after cycling. In contrast, 3D GF-Cu favors low voltage polarization due to the larger surface area of the porous Cu, which can reduce the practical current density and restrict Li plating within the pore space reserved for Li accommodation.

Li|LiFePO₄ full battery tests were performed (Figure 5d) using bare Li metal and 3D GF-Cu@Li at 0.5 C. Slight capacity increase in the first few cycles is due to the activation process of the LiFePO₄ materials. The 3D GF-Cu@Li cells exhibited an improved cycling stability, which retained 91% of their initial discharge capacity after 200 cycles with the stable CE of 99.5%. In comparison, the bare Li metal showed more evident capacity fading, which only delivered 81% of initial discharge capacity at 200th cycle.

We also investigated the electrochemical performance of the other current collectors derived from different matrix shown in Figure 1. Substrates with different pore structures have a great influence on the CE stability. The CE stability of commercial Ni foam with large pore diameters range from 200 to 400 μ m was even worse than that of the 2D Cu, which exhibited a continuous degradation after 50 cycles. SEM images in Figure S7a (Supporting Information) of the 50th Li plating and stripping indicated that although Li metal can fill in the foam pores, much of the inserted Li cannot get out of the Cu coated Ni foam, forming dead Li with large irreversible capacities. In contrast, polyether, polycarbonate objects with pore sizes that are too small (100-200 nm) act much like the planar 2D current collectors, since most of the deposited Li metal was found on the surface (Figure S9b, Supporting Information). Additionally, excellent mechanical stability is also necessary to construct an ideal 3D current collector. Consequently, rice paper substrates present an average CE over 90% over 100 cycles at 0.5 mA cm⁻², but drops below 70% after 50 cycles at higher rates such as 1 and 2 mA cm⁻². Strong conductive 3D current collectors derived from the matrixes with proper pore structures of GF, polycarbonate (PC), polyethylene terephthalate (PETE) with pore size range from 400 nm to 1 µm achieved better cycling performance.

3. Conclusion

In summary, we presented a new method of developing "transform" 3D conductive frameworks based on cheap and







Figure 5. Voltage profiles in symmetric Li|Li@Cu cells with a) 3D Cu foil or b) planar Cu. c) Average voltage hysteresis of Li metal plating/stripping at 0.25 mA cm⁻². d) Cycling performances of an Li anode with 2D and 3D current collectors in a full cell with an LiFePO₄ cathode at 0.5 C.

common materials to solve the lithium dendrite problem. PDA coatings form on nearly all types of material surfaces, giving an extremely versatile and highly effective platform for secondary metal coatings. This dip-coating method can virtually turn every porous material, ranging from metal to semiconductor to insulator, into an effective 3D current collector. This method includes cost-effective compounds and operates under mild reaction conditions, making it highly competitive for scale up. The 3D conductive architecture with large specific surface area can greatly reduce the ion flux density and provide enough sites for homogenous Li nuclei distribution and growth. The porous scaffold also acts as a rigid host to accommodate the volume change of the Li metal. Hence, this 3D current collector maintains an enhanced CE of 94% for 600 h at 0.5 mA cm⁻² and long-term cycling stability is demonstrated in full batteries (Li@3D GF-Cu|LiFePO₄). This facile and versatile strategy of metal coating makes a great step towards building an ideal scaffold for Li encapsulation and enormously broadens the choices of suitable 3D porous materials for hosting the Li metal.

4. Experimental Section

PDA Coating: The dopamine is a small molecule with both catechol and amine functionalities, a simple mimic of Mytilus edulis foot protein.

The protein is rich in 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine amino acids and performs an important role in mussels' adhesive ability. Dopamine could participate in reactions of bulk solidification and form strong covalent and noncovalent interactions with substrates. Dopamine solution was obtained by dissolving dopamine into 10×10^{-3} M Tris-HCL (pH = 8.5). In order to have a compact structure after solution soaking, the GF substrate was heated in air at 500 °C for 2 h before use. After dipping the substrates into the aqueous dopamine solution, dark brown color was observed over time. The thickness of the PDA coating is a function of the immersion process and can be reached up to 50 nm after 24 h.^[15a] As a result, the immersion process was continued for 24 h to ensure the formation of the PDA coating on substrates. The as-immersed substrates were washed with distilled water and dried at 60 °C.

Electrode Metallization: An aqueous solution of 50×10^{-3} m CuCl₂, 0.1 m H₃BO₃, 50×10^{-3} m ethylenediaminetetraacetic acid (EDTA) was prepared, followed by a pH adjusting process with 1 m NaOH until the pH was 7. Before dipping the PDA coated substrates into the solution, 0.1 m dimethylamine-borane (DMAB) was added. The substrates were kept in the solution for 6 h at 35 °C and then 12 h at room temperature. Again, the Cu coated substrates were rinsed with distilled water and dried at 60 °C under vacuum. The mechanical robustness of the as-prepared electrodes is demonstrated in Figure S1 (Supporting Information).

Electrochemistry: All batteries were carefully prepared in the glove box with a Swagelok cell configuration. 3D copper electrode and 2D copper foil were assembled and tested with lithium metal as anode and Celgard 2500 as separator. Batteries were cycled at different current densities ranging from 0.5 to 1.5 mA cm⁻² with the capacity of 1 mAh cm⁻². Lithium was firstly deposited on the copper electrode for 1 mAh cm⁻² and then charged to 0.5 V to delithiate from the copper electrode.

For the symmetric battery test, a prelithiation process was firstly conducted using a lithium metal as anode. The lithium metal was then replaced by a new copper electrode. The batteries were charged and discharged for 1 h at current density of 1 mA cm⁻².

For the full battery test, LiFePO₄ cathode was prepared by coating an active material (80 wt%), carbon black (10 wt%), and polyvinylidene difluoride (PVDF) (10 wt%) solution (in N-methylpyrrolidone (NMP)) on an Al foil and then dried under vacuum. The prelithiated 3D copper was cycled with LiFePO₄ as a counter electrode at 0.5 C. EC/DEC (1 $\mbox{M LiPF}_6$) was used as electrolyte in all batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D conductive framework, Cu coating technique, dendrite suppression, lithium metal anodes

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