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Horizontal Stress Release for Protuberance-Free Li Metal Anode

Yuanming Liu, Xiaoguang Yin, Xin Shen, Peichao Zou, Xianying Qin,* Cheng Yang, Qiang Zhang, Feiyu Kang, Guohua Chen, and Baohua Li*

Dendrite-induced short circuit and capacity loss present major barriers to high-energy-density lithium (Li) metal batteries. Many approaches have been proposed to regulate or restrain the formation of Li dendrite, yet it has not been fully eliminated. Herein, a dredging tactic with hemisphere-like concaves is designed to horizontally release the stress during Li deposition, making both upper smooth Li and nether granular Li dwell inside the compartmented tummy. With such protuberance-free Li metal anode, an ultrahigh Coulombic efficiency over 96% of the half-cell is maintained after 490 cycles and capacity retention of 100% for the full cell paired with a LiFePO₄ cathode after 140 cycles (with low N/P ratio of \approx 5) is achieved simultaneously. This study contributes to a deeper comprehension of electrochemical metal deposition and promotes the development of safe batteries.

1. Introduction

With the fast-growing demand of electronic devices and vehicles, traditional lithium (Li) ion batteries can no longer satisfy the application requirements for high-density energy storage.^[1-4] Therefore, Li metal based rechargeable batteries including Li– sulfur (S), Li–air, and Li–selenium (Se) batteries have made a strong comeback and attracted a heap of attentions because of their higher energy densities.^[1,2,5–8] In spite of the successful

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use in primary batteries, Li metal anode presents a poor cyclability and low Coulombic efficiency in secondary batteries, as well as encounters severe safety concerns caused by the perpendicular growth of Li dendrites.^[1,2,9] Efforts toward addressing these issues so far mainly focused on dendrite-growth-delay and -suppression strategies via the employments of optimized electrolyte,^[10] modified separators,^[11,12] Li surface modifications,^[13,14] artificial anode surface coatings,^[15-17] nano- and microstructured porous current collectors,^[6,18–20] etc. Despite numerous efforts have been made to restrain the dendrite formation, the emergence of Li dendrites cannot be completely avoided during prolonged

cycling, especially when batteries are operated in overcharge ultimate or at low operation temperatures. $^{[2,19]}$

The lithiophilic nature of current collector is one of the dominant factors for uniform Li deposition. Therefore, heteroatom doping in substrates, focusing on nitrogen-doping,^[21] oxygendoping,^[22] and phosphorus-doping,^[15] have been carried out to realize the homogeneous Li metal nucleation. More recently, the selective Li deposition can be realized on the faceted Cu (100) surfaces, because the Cu (100) surface is lithiophilic for Li deposition via the Li (110) oriented Li layer.^[23–25] Although the initial nucleation process can be largely improved by altering the lithiophilicity of the current collectors, the almost infinite volume expansion and shrinkage are ineluctable for the Li metal deposition, especially under the circumstance where large amount of Li is needed.

Furthermore, very few researches have been carried out to resolve the plating induced stress in Li metal and the related effect on Li deposition morphology.^[7] Since residual stress is ubiquitous in the random Li plating process, it is logical to ask whether this undesirable phenomenon can be alleviated through effective methods. In fact, the compressive stress caused by the random Li plating cannot be fully relaxed and a certain amount of Li dendrites may emerge anywhere on the plating surface.^[2,7,26] Typically, in a sandwich structured cell, a separator is placed between anode and cathode.^[4,8,27,28] The perpendicular Li dendrites formation would be hindered to some extent, because of the mechanical strength of separator.^[29] However, when there is a large amount of Li dendrites, the localized stress concentration caused by the dendrite would pierce the separator, causing the short circuit of battery.^[27] Thus, another directing way was designed by modulating the

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growth direction of dendrites parallel to the separator.^[19] However, the large amount of formed Li dendrites would cause the fast consumption of both Li metal and electrolyte, resulting in the shortened cycle life.

Herein, with the aim to control the dendrites direction and alleviate the stress induced by Li plating at the same time, the tangent and lithiophilic hemispherical concaves was designed and fabricated for Li metal deposition. On the one hand, the Cl⁻ selective etching for Cu matrix formed the Cu (100) crystal phase dominated hemispherical concaves, which is pivotal for the prior nucleation of Li metal into the holes. Moreover, the etching caused nano- and microhybrid rough surface inside the hemispherical holes would help to homogenize the ion distribution and lead to uniform Li metal deposition, which was further testified by the simulation in COMSOL Multiphysics. On the other hand, in practical cell system, a selfsuppressed Li metal growth mechanism was realized by the stress release mechanism through the edge of hemisphere and platform. Experimental investigations combined with numerical simulations are performed to evaluate such a unique current collector for Li metal in the cell configuration. The resulted Li metal electrode could maintain a Coulombic efficiency over 96% after 490 cycles at 1 mA cm⁻². Even at a high Li capacity of 4 mAh cm⁻², it could also deliver a Coulombic efficiency of 96% after 100 cycles. And the resulted Li metal anode could also show a much-improved full cell performance when matched with the LiFePO4 (LFP) cathode with a low N/P ratio ≈ 5 . This work develops the structure design for Li metal anodes and delivers a deep understanding of Li metal electrodeposition.

2. Results and Discussion

The tangent and lithiophilic hemispherical (TLH) electrode was fabricated via a series of processes, including hot lamination, laser ablation, alkaline etching, and removal of PI films, as schematic in Figure 1a. During the hot lamination process, a Planar Cu foil was sandwiched between two PI films. Then, laser ablation was utilized to prepare the pinholes with cubic lattice. The alkaline Cl⁻ etching was carried out subsequently. Finally, the TLH Cu electrode was obtained after the removal of two layers of PI film. The scanning electron microscope (SEM) images of the resulted TLH-300 electrode which has a hemisphere diameter of 300 µm were shown in Figure 1b-d. As shown in Figure 1b,c, tangent cupped hemispheres are homogeneously distributed on the TLH electrode, while unetching separated flats remained between these etching-caused hemispheres. Moreover, the high-resolution SEM image of the etching caused hemisphere (the inset in Figure 1d) shows a rough surface, which increases the specific surface area of electrode. And it is beneficial to regulating the ion distribution and inducing a uniform Li deposition.^[6,18,30] More recently, Gu at al reported that the Cu (100) faceted surface is more lithiophilic than other crystallographic surfaces of Cu.^[24] Due to the strong adsorption of SO_4^{2-} on the Cu (111) face and the preferred adsorption of Cl⁻ on the Cu (100) one, the electrodeposited Cu would turn the Cu (111) dominated surface to the Cu (100) faceted one in the chloride-containing sulfuric acid solution. In this research, we choose the Cl⁻ containing etching solution to orient the etch process. Specifically, during the etching process, the Cl⁻ would be adsorbed on the (100) face of Cu, and thus



Figure 1. a) Schematic illustration of the fabrication process of TLH electrode; b) front SEM image of the TLH-300 electrode (the insets are the two main parts of the front side of TLH electrode); c) cross-sectional SEM image of the TLH electrode (the inset is the SEM in higher magnification); d) SEM image of the obtained lithiophilic hemisphere of TLH electrode (the inset is the surface rough structure caused by the isotropic Cl⁻ etching); e,f) X-ray diffraction (XRD) patterns of Planar Cu and TLH-300 electrodes respectively; g) CV curves of Li | Cu and Li | TLH-300 half cells scanned at -0.3 to 3V, 20 mV s⁻¹.





the etching process along the (100) face would be impeded to some extent. The X-ray diffraction (XRD) patterns of the pristine electrode (Planar Cu) and the etched electrode (TLH-300) are shown in Figure 1e,f, respectively. As shown in Figure 1e, for the pristine Planar Cu foil, the ratio of the relative intensity of the plane (200) to (111) is 1.073. However, after the isotropic etching process, the ratio is increased to 5.293, though there still exist a quarter of pristine flat on the TLH electrode. The significantly improved relative intensity of plane (200) is the direct evidence for the lithiophilicity of etching-caused cupped hemispheres. Further, for the CV curves of Li | Cu half cells, the Li | Planar Cu cell delivers a delayed Li plating dynamics (\approx 119.8 mV) compared with the Li | TLH-300 cell (\approx 79.4 mV). The increased current response on the TLH-300 electrode means the rapid Li⁺ transport and reversible reaction kinetics originating from the (100) faceted lithiophilic hemisphere.^[24,25]

To verify the deposition of Li in TLH electrode, we simulated the current density distribution using COMSOL Multiphysics, as shown in Figure 2d–f. First, the porous substrate increases the interfacial area for electrochemical reactions, thus reducing the deposition current density compared with the flat substrate. Moreover, the lightning rode effect could result in a higher current density at the intersection of flat surface and hemisphere. However, this effect could be largely alleviated by the roughness of the etched surface of inner hemisphere, as revealed by Figure 1d. From Figure 1d, the roughness can further increase interface area in comparison with geometry of smooth pore surface. Therefore, electrodeposition would be triggered around small roughness due to the prior current density distribution in the rough pore structure. It is worth noted that with the ascending of roughness size from 0 to 20 µm, the current density tends to distribute into the hemisphere rather than the flat surface (Figure 2d-f and Figure S3, Supporting Information). Considering the dimensions of our Cu (100) dominated hemisphere is around 10 nm to 1 µm, which is the mixture of micro- and nanostructure and shows higher specific surface area. Therefore, the TLH electrode is effective in regulating the Li ion distribution during the electrochemical deposition of Li metal. Further, the lithium deposition process was recorded by in situ optical microscopy. The surfaces of both the Planar Cu and TLH-300 electrodes are smooth without obvious Li protuberances during the initial deposition stage. Irregular and bulk dendritic Li deposits on the Planar Cu electrode after 30 min at 1.0 mA cm⁻² (Figure 2g), which is caused by the inhomogeneous Li⁺ distribution during initial Li nucleation. However, for the TLH-300 electrode, due to the rough surface and Cu (100) faceted lithophilic feature of the hemispheres, the Li tends to nucleate at the inner pores and then gradually spread over the whole front surface (Figure 2h). Subsequently, followed by the homogeneous Li⁺ ions distribution induced by the primary deposited Li, the incoming Li⁺ ions can deposit uniformly on top of the TLH electrode, resulting in a flat Li layer ultimately.

For the Planar Cu electrode with small surface area, a large number of nonuniform Li nucleus are deposited, which provide more hot spots for Li dendrite formation. As a result, uneven Li



Figure 2. a) Simulated ion distribution of single hemisphere of TLH-300 electrode; b) electrical field distribution of the TLH-300 electrode; c) schematic illustration of the more uniform ion distribution of the etching caused TLH-300 electrode; Current density magnitude (A m⁻²) distribution (with the electrolyte layer of 650 μ m) at 0 s for four geometry (from left to right in the order of different sizes of roughness of 0, \approx 1, \approx 5, and \approx 20 μ m): d) pristine result, e) only domain with current density magnitude greater than 8.5 A m⁻² and f) only domain with current density magnitude greater than 9.99 A m⁻² are shown; g,h) in situ optical observations of the Li metal deposition process on planar Cu and TLH-300 electrodes at 1 mA cm⁻², respectively.





deposits with moss- or dendrite-like morphology are distributed on the Planar Cu. By contrast, for the TLH current collector, the rough surface of the tangent hemisphere generated by isotropic etching increases the specific surface area efficiently, thus the uniform Li deposits are expected not only on the surface but also in the microchannels (Figure 2a–c).

Nevertheless, although the electrodeposition of Li metal on the TLH electrode is flat and uniform, it is still inadequate in manifesting its high efficiency in practical cells. Indeed, a piece of separator is a must for the normal cell operation, which is different from the electrodeposition circumstance (**Figure 3**a,n). Particularly, the separator can transmit pressure to the newly deposited Li, thus the Li metal tends to deposit more uniform and large-sized.^[26] Herein, to characterize the effect of pressure between the separator and electrode for the Li metal deposition, the Li | Cu half cells with different packaging pressure (i.e., posing different pressure between separator and electrode) were fabricated first to characterize this effect, as shown in Figure 3b–m. When the packaging pressure of Li | Cu half cell is only 30 MPa (Figure 3b–d), the Li metal deposits to be dendritic and nonuniform on the Planar Cu electrode. The deposited Li is smoother than the electrodeposition morphology (Figure 2g), and in distinct contrasting to the "free style" growth metallic Li. When the packaging pressure further increasing to 40 MPa, the dendritic Li deposition could be further inhibited (Figure 3e–g). Moreover, the Li metal tends to deposit more uniformly and compactly if the packaging pressures of 50 MPa (Figure 3h–j) and 60 MPa (Figure 3k–m) are loaded. The compressive stress between the separator and electrode could let the Li deposition morphology smoother, which is in distinct difference to the



Figure 3. a) Schematic illustration of the difference between free style deposition and cell style deposition using planar Cu electrode, and cell style Li deposition morphologies on planar Cu electrode (2 mAh cm⁻² at 1 mA cm⁻²) under different packaging pressure b–d) 30 MPa; e–g) 40 MPa; h–j) 50 MPa; k–m) 60 MPa; n) schematic illustration of the surface geometry of TLH electrode (the flat surface contributes the 21.5% of the surface area), and the difference between free style deposition and cell style deposition using TLH electrode, and cell style Li deposition morphologies on TLH-300 electrode (6 mAh cm⁻² at 1 mA cm⁻²) under different packaging pressure o–q) 30 MPa; r–t) 40 MPa; u–w) 50 MPa.

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electrodeposition morphology observed by in situ optical cell (Figure 2g).

The pressure is also significant for the Li plating on TLH-300 electrode, as shown in Figure 3o-z. With the packaging pressure increasing from 30 to 60 MPa, the deposited Li on the flat surface of TLH-300 electrode delivers a more and more smoother morphology (Figure 2h). The dense Li plating on the flat surface of TLH-300 electrode originates from the compressive stress between the separator and electrode. However, apart from the packaging caused macroscopic compressive stress, the microscopic residual stress is also ubiquitous and significant during the metal plating process. As reported by Wang et al.^[7] the presence of compressive stress during plating could promote the Li dendrite formation, and the dendrite formation could be alleviated by relieving the residual stress. For the Planar Cu electrode, after adding a separator, the formation of dendritic Li in the perpendicular direction could be largely inhibited (Figures 2g and 3b-m), because of the imposed stress between separator and electrode. However, due to the horizontal compressive stress of Li metal itself and the vertical stress between deposited Li metal and separator, the formation of dendritic Li would be serious during the repeated Li plating/ stripping process. However, for the TLH electrode, it is mainly composed of the flat surface and the etching caused lithiophilic hemispheres. During the electrochemical Li depositing process, the incoming Li ions would nucleate at the inner surface of hemisphere firstly due to its rough surface structure and lithiophilic nature. However, the Li metal would also deposit onto the flat surface of TLH electrode just following. It is worth noting that the separator of the Li | TLH cell could only get attach with the flat surface of TLH electrode, thus the compressive stress between the separator and the flat surface of TLH electrode is ≈4 times the stress of Planar Cu electrode in theory. In consequence, during the Li plating process, the Li plating morphology could be smoother than Planar Cu electrode with the help of this stress.

Specifically, the plating induced compressive stress of Li metal could be largely released by way of lateral growth along the edge of hemispherical concave and flat surface of TLH electrode. To figure out the horizontal Li metal plating mechanism, the surface geometry of TLH electrode was systematically analyzed, as shown in the Part S1 of the Supporting Information. By the geometry analysis of TLH electrode, the total length (i.e., the total edge of the hemisphere and flat surface of TLH electrode) could be largely increased compared to the perimeter of the Planar Cu electrode. This is helpful in regulating the horizontal Li metal growth. For example, with the electrode diameter of 12 mm and the hemisphere diameter of 0.3 mm, the total length for horizontal growth on TLH electrode is 32.4 times of pristine Planar Cu electrode. With decreasing the hemisphere diameter from 0.3 to 0.25 mm, and finally to 0.2 mm, the ratio could be increased from 32.4 to 38.7, and finally to 48.1, respectively. It manifests that the smaller the hemisphere is, the more effective the TLH electrode is in relieving the deposited stress of Li metal. However, with the smaller hemisphere, the volume to resolve Li would be lesser. With the Li capacity of 1 mAh cm⁻², there is only a small number of Li deposit on the flat surface of LTH-300 (Figure 4a-e) due to its smaller overlap area than hemisphere (Figure 3n).



When the Li amount increases to 2 mAh cm⁻², the flat Cu surface of TLH-300 electrode could be fully covered by Li metal (Figure 4f-j). Though the Li amount deposited within the hemisphere increases, it is still caged inside the hemisphere without protruding out of the concave structure. When the Li capacity further increases to 6 mAh cm⁻² (Figure 4k-o) and 10 mAh cm⁻² (Figure 4p-t), the deposited Li on the flat surface could both maintain a smooth and dense structure. Moreover, the Li metal plated on the flat surface could become wider and thicker with the Li deposition (Figure 4c,h,m,r and d,i,n,s), and Li metal deposited inside the hemisphere would fill in the concave step by step (Figure 4e,j,o,t). The plating behaviors of Li metal on Planar Cu and TLH electrodes are shown in Figure 4u,v, respectively. The coupling of flat and concave structure of TLH electrode is effective to release the compressive stress originated from Li deposition and reserve the horizontal dendrites, thus resulting in the self-suppressed Li metal deposition.

To further characterize the reversibility of repeated Li plating/ stripping, the crucial factor-Coulombic efficiency has been adopted to evaluate the electrochemical performance of TLH electrode. Typically, the Coulombic efficiency was defined as the ratio of Li stripping capacity to plating one. In this research, the Coulombic efficiency was measured with plating a definite capacity of Li at a given current density and then charging up to 1 V (vs Li⁺/Li) for cycles, as illustrated in Figure 5a-c. When the deposition capacity of Li was 1 mAh cm⁻² at a current density of 1 mA cm⁻², the TLH-300 electrode could deliver a high initial Coulombic efficiency of 92.7%, 96.1%, 94.9%, and 95.3% with the packaging pressure of 30, 40, 50, and 60 MPa, respectively. After being repeatedly plating/stripping Li metal for 200 cycles, only the TLH-300 electrode with the packaging pressure of 50 MPa could maintain a high Coulombic efficiency of 97.7% (while 83.8% for 30 MPa, 86% for 40 MPa, 85.2% for 60 MPa), which indicated that despite the deposition morphology could be altered by increasing the packaging pressure, the actual electrochemical performance may not show an upward trend with the increasing of packaging pressure all the time. More profoundly, the TLH-300 electrode could still retain an ultrahigh Coulombic efficiency of over 96% after being cycled for 490 cycles. When the Li capacity further increase to 4 mAh cm⁻², it showed the same trend either. The TLH-300 electrode with packaging pressure of 50 MPa could maintain a Coulombic efficiency of 95.7% after being cycled for 100 cycles, which was in stark contrast to other conditions (78.2% after 50 cycles for 30 MPa, 84.4% after 68 cycles for 40 MPa, and 78.2% after 77 cycles for 60 MPa). While the Planar Cu electrodes with packaging pressure of 50 MPa could only retain a Coulombic efficiency of 73.28% after 118 cycles and 68.8% after 48 cycles with the Li capacity of 1 and 4 mAh cm⁻², respectively. The TLH-300 electrode could induce the homogeneous Li deposition due to the existence of lithiophilic rough hemisphere (Figure 2h), thus it delivered improved electrochemical performance than Planar Cu electrode. However, for the conditions where different packaging pressures were employed, the TLH-300 electrode showed totally different Li plating/ stripping behaviors. The best electrochemical performance was obtained under 50 MPa packaging pressure. The performance started to decay when further increase the pressure to





Figure 4. SEM characterizations the Li deposition morphologies on TLH-300 electrode with different amount of Li with the same packaging pressure (50 MPa) at 1 mA cm⁻²; a–e) 1 mAh cm⁻²; f–j) 2 mAh cm⁻²; k–o) 6 mAh cm⁻²; p–t) 10 mAh cm⁻²; u,v) schematic illustration of the cell style Li deposition mechanisms of planar Cu and TLH electrodes, respectively.

60 MPa. We speculate this is result from the limited mechanical strength of polymer separator. We do agree that the preset pressure between separator and electrode is beneficial for uniform Li deposition, especially for TLH electrode showing self-suppressed Li metal deposition. However, the excessive pressure between the separator and electrode may cause an ultrahigh stress load for the separator, and is harmful for the long-term cycling performance. That is the reason why many researches using glass fibers,^[11,31] artificial solid state interface (SEI),^[14,32] gel polymer,^[16] and solid state electrolyte^[33] as the separator or both the separator and electrolyte. Moreover, with the Li capacity further increasing to 2 mAh cm⁻² at a higher current density of 4 mA cm⁻², where the stress caused by Li metal deposition would be more severe, the TLH electrodes with different diameters showed different capabilities in releasing the deposition inducing stress, as shown in Figure 5c. As discussed before, the smaller the diameter of the hemisphere is, the more effective the TLH electrode in reliving the stress resulted from the Li metal deposition. The TLH-200 electrode delivered the initial Coulombic efficiency of 95.8% and a value of 94.1% after 50 cycles at current density of 4 mA cm⁻². While the TLH-250

and TLH-300 electrodes could only maintain the Coulombic efficiency of 90.4% and 81.2% after 50 cycles, respectively, which was in distinct contrast to the TLH-200 electrode. The enhanced electrochemical performance of TLH-200 electrode under ultrahigh current density (4 mA cm⁻²) manifested the superiority of the tangent lithiophilic hemisphere induced self-suppressed lithium metal anode.

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Symmetrical cells were also assembled to evaluate the longterm stability upon Li plating/stripping with a fixed capacity of 1 mAh cm⁻² at the specific current density of 1 mA cm⁻². Prior to the test, 3 mAh cm⁻² of Li was plated onto the working electrode at 1 mA cm⁻². From the voltage–time curves shown in Figure 5d, the TLH-300 electrode presented a long-term stability up to 650 h, while the cell with Planar Cu current collector only showed a gradual hysteresis augment over cycles (250 h) and a fluctuant cycling plateaus in both Li deposition and dissolution processes. Moreover, full cells were also fabricated by assembling the commercial LiFePO₄ (LFP) cathode with the plated Planar Cu @ Li and TLH-300 @ Li, respectively. The cyclic stabilities were investigated at 0.5 C (based on the theoretical capacity of LFP), as shown in Figure 5e. The





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Figure 5. Coulombic efficiencies of a,b) planar Cu electrode with packaging pressure of 50 MPa, and TLH-300 electrode with packaging pressure of 30, 40, 50, and 60 MPa at 1 mA cm⁻² with Li capacity of 1 and 4 mAh cm⁻², respectively; c) Coulombic efficiencies of planar Cu electrode and TLH electrodes with different diameters of the hemisphere under the same package pressure (50 MPa) at 4 mA cm⁻² with Li capacity of 2 mAh cm⁻²; d) symmetrical cell test of planar Cu and TLH-300 electrodes at 1 mA cm⁻² with Li capacity of 1 mAh cm⁻²; e) cycling performance of the Li deposited planar Cu and TLH-300 electrodes matched with N/P ratio of \approx 5); SEM images of the cycled morphology of f–h) planar Cu after repeated Li plating and stripping 200 cycles and i–k) TLH-300 electrodes after repeated Li plating and stripping 200 cycles at 1 mA cm⁻² with Li capacity of 1 mAh cm⁻², respectively.

TLH-300 @ Li full cell showed an area discharge capacity of 0.90 mAh cm⁻² at the first cycle of 0.5 C, and could still maintain 0.90 mAh cm⁻² after being operated for 140 cycles, corresponding to the capacity retention of 100%. However, for the circumstance of Planar Cu @ Li anode, it could only deliver an initial area discharge capacity of 0.87 mAh cm⁻² and a following value of 0.80 mAh cm⁻² at the 140th cycle, which corresponded to the capacity retention of 92%. Additionally, the Planar Cu @ Li | LFP full cell could only deliver an average Coulombic efficiency of 98.8% within 140 cycles at 0.5 C, far bellowing

the average Coulombic efficiency of 99.8% for TLH-300 @ Li | LFP full cell. The morphologies of the cycled Planar Cu and TLH-300 samples at 1 mA cm⁻² were characterized by SEM, as shown in Figure 5f–h and i–k. The cell using Planar Cu delivered a loose structure with superficial lithium dendrites, which explained its fast decay of Coulombic efficiency. While the TLH-300 electrode exhibited a uniform and dense SEI layer covering the electrode surface even after 200 cycles, revealing no mossy Li on the surface. The electrochemical characterizations and cycled morphologies demonstrated that the enhanced SCIENCE NEWS _____ www.advancedsciencenews.com

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Li plating/stripping kinetics and more stable electrode interface could be achieved through the novel structure and function design for TLH electrode.

3. Conclusion

In summary, the present work incorporates a scalable technology to fabricate the tangent lithiophilic hemisphere structure to realize the uniform Li deposition in both electrochemical freestyle deposition and bound deposition. Typically, the geometry of the obtained TLH electrode affected the current density distribution, Li morphology evolution, and its electrochemical performances in the half and full cells. Moreover, a novel Clselective etching method for Cu to fabricate the Cu (100) dominated structure was proposed to augment the lithiophilicity of current collector. Therefore, a uniform freestyle Li deposition could be achieved. Meanwhile, a self-suppressed Li metal deposition mechanism was realized in practical cell system when using such a TLH electrode. Therefore, the resulted Li metal anode could maintain a Coulombic efficiency over 96% after 490 cycles and 95.7% after 100 cycles with Li capacity of 1 and 4 mAh cm⁻², respectively. The prolonged cycle life and capacity retention of the full cell with low N/P ratio could also be achieved when paired with LFP cathode. Our findings here provide mechanistic insights into the stress releasing during Li metal deposition. This unique structure deepens the design of Li metal anodes and could deliver an insight understanding of the Li metal deposition.

4. Experimental Section

Preparation of TLH Concave Electrode: The preparation process was based on a primary reported method including a series of process, namely hot lamination, laser ablation and alkaline etching.^[19] Typically, two PI films with a thickness of 25 μ m were separately coated onto both surface of a commercially available planar Cu foil (200 μ m in thickness) via hot lamination at 180 °C. Subsequently, the pinhole array (diameter of 300, 250, 200 μ m) was produced via a laser ablation process with a nanosecond pulsed laser (EP-15-DW, Han's Laser Technology Co., Ltd. China). Next, the PI-clad copper foil was immersed into an alkaline etching solution (Copper ammonia solution) to allow the isotropic etching of the inner copper foil to obtain PI coated TLH electrode. Finally, after tearing off the PI layers, the eventual TLH electrode could be used as current collector for Li metal. Herein, the copper ammonia solution was composed of 1 $\,{\mbox{\scriptsize M}}$ CuCl_2 and 0.5 $\,{\mbox{\scriptsize M}}$ NH_4Cl, and the pH of the solution was tuned to 8 via adding NH₃·H₂O. It is worth special mentioning that the $\mathsf{C}\mathsf{I}^{\!-}$ selective etching of the etching solution could result in a Cu (100) dominated etching surface, due to the prior adsorption of Cl⁻ on the Cu (100) surface during the reaction process.^[24]

Characterization: SEM (Cold Field Scanning electron microscope (SU8010, HITACHI)) was utilized to characterize the morphology of TLH current collector, lithium deposition morphology, and cycled morphology. XRD (Bruker D8 Advance system using Cu K_a radiation (λ = 0.154 nm, tube voltage: 40 kV and tube current: 40 mA) was adopted to explore the etching surface structure of TLH and Planar Cu electrodes. As it is known, XRD is a technique with the detection depth about several micrometers. In this case, the etching caused micro- and nanohybrid structure of TLH electrode showed the thickness of several micrometers and which is comparable to the detection depth of XRD. Therefore, the XRD characterization could acquire the faceted information of the Planar Cu and TLH electrodes. In situ observations were carried out

in a home-made optical cell with quartz window for observation. Both the Li metal and the current collector were placed into the cells. After injecting electrolyte, the cell was sealed with fluorine rubber ring. The assembly of optical cell was performed at room temperature in an Argon-filled glovebox with water and oxygen content less than 1.0 ppm. Optical microscope with a fitted charge coupled device (CCD) camera was applied to shoot the Li deposition process.

Electrochemical Testing: With the aim of evaluating the performance of repeated Li plating and stripping on TLH current collector, the TLH current collector (with diameter of 12 mm) was used to assemble a CR2032 coin cell using Li foil (≈580 µm, which corresponds to 120 mAh cm^{-2} of Li) as counter electrode and Celgard 2400 as separator. The electrolyte was 1 м bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) dissolved in a mixture of 1,2-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume) with 1 wt% lithium nitrate (LiNO₃) as the additive. Typically, 70 µL of electrolyte was added into the coin cell for further characterization. The Coulombic efficiency was tested on a Land 2001A cell test system (Wuhan, China). Prior to the test, the cell was cycled at 50 μ A between 0.01 and 1V (vs Li⁺/Li) for 5 cycles to form a stable SEI. Then a certain amount of Li was electroplated on the samples at specified current density, followed by stripping up to 1 V (vs Li⁺/Li) at the same current density for each cycle. The symmetric cell tests were also firstly cycled at 50 µA between 0.01 and 1 V (vs Li⁺/Li) for 5 cycles. Then, 3 mAh cm⁻² of Li was plated on the electrode at 1 mA cm⁻², following the repeated Li striping and plating at 1 mA cm⁻² for 1 h for each semicycle. For full cell tests, the commercial purchased LiFePO₄ was chosen as cathode. The LiFePO₄ powder, poly(vinylidene fluoride) (PVDF) and super P were mixed in NMP with mass ratio of 8:1:1, and then casted on an aluminum foil followed by vacuum drying for 12 h at 110 °C. The average mass loading of LiFePO₄ in the electrode was ≈6 mg cm⁻². The 2D planar Cu or TLH current collector was first assembled into a half cell using a Li foil as counter electrode. The electrolyte used here was 1 M lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (in a volume ratio of 1:1) with 10% of fluoroethylene carbonate (FEC). After depositing 5 mAh cm⁻² of Li metal onto the current collector at a current of 1 mA cm $^{-2}$, the cell was disassembled in an Ar-filled glove box and the newly deposited Li anode was further reassembled into a full cell against LiFePO₄ cathode using the same electrolyte. The cell was galvanostatically cycled between 2.4 and 4.2 V at 0.5 C after activation for 1 cycle at 0.1 C based on the theoretic capacity of LiFePO₄ (170 mAh g^{-1}).

Numerical Simulation: The numerical simulations of the ion distribution on the TLH current collector were conducted on COMSOL Multiphysics. The coupled "Tertiary Current Distribution, Nernst-Planck" module and "Deformed Geometry" module are employed. Computational domain changes as Li deposits onto Cu substrate. Deposition in 2D geometry with symmetric side boundary conditions is simulated, see Figure S1 in the Supporting Information for smooth pore with radius of 150 μ m. Different sizes of roughness are generated on the pore surface, see Figure S2 (Supporting Information). The diffusion coefficient of Li⁺ (D) was set to 2×10^{-9} m² s⁻¹. The initial electrolyte concentration (C₀) is set to 10³ mol m⁻³ (1 mol L⁻¹), and the inward current density at cathode (*i*_{bc}) is 10 A m⁻² (1 mA cm⁻²).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

horizontal growth, stress release, hemisphere-like concaves, protuberance-free anodes, lithium metal batteries

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