Graphene anchored on Cu foam as a lithiophilic 3D current collector for a stable and dendrite-free lithium metal anode†

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Lithium (Li) metal has been considered as the most promising anode material for high-energy-density batteries. However, its practical application has been affected by the growth of dendrites and volume change, which results in low coulombic efficiency (CE) and safety concerns during repeated Li plating/stripping. Herein, we show that a 3D current collector with graphene anchored on copper foam (GN@Cu foam) can induce uniform and stable Li deposition over a wide current density range and long-term cycling. It can maintain a CE of 97.4% for 150 cycles at a current density of 2 mA cm$^{-2}$ in half cells and afford an areal capacity of 6 mA h cm$^{-2}$ at 6 mA cm$^{-2}$ in symmetric cells. When cycling at 0.5 mA cm$^{-2}$, the current collector presents a CE as high as 98.6% for 250 cycles in half cells and a low voltage hysteresis of 10 mV over 2000 h in symmetric cells. The GN@Cu foam serves as a conductive skeleton with moderate specific surface area and lithiophilic sites to store Li, exhibiting a dendrite-free morphology after long term cycling. This study provides novel insights into modifying a 3D current collector with lithiophilic materials towards an advanced and stable Li metal anode.

Introduction

The increasing demands of high-energy-density batteries for advanced electronic devices continue to stimulate research interest in Li metal anodes due to its extremely high specific capacity (3860 mA h g$^{-1}$, one order of magnitude higher than that of graphite) and low reduction potential (−3.04 V vs. the standard hydrogen electrode).1,1 Unfortunately, the formation of dendritic Li metal and the significant volume changes during repeated Li plating/stripping processes are safety hazards and result in the collapse of the solid electrolyte interface (SEI), which is fatal to battery operation and performance, thus preventing the practical application of Li metal anodes.6,7 Accordingly, great efforts have been devoted to solving these critical challenges in different ways, such as introducing electrolyte additives to stabilize SEI,7,9 applying artificial SEI or protective layers,10–18 modifying separators19–21 and designing 3D current collectors.19,22,24 Among these methods, constructing 3D current collectors as host materials for Li is attractive because the 3D substrates can not only regulate Li plating and accommodate volume changes, but also decrease the local current density because of the enlarged surface area.25–27 As a result, they are beneficial to the improvement in interface stability and delay in the formation of dendrites according to Sand’s time model.28,29

Compared with SEI layer design, 3D current collectors fundamentally suppress the growth of dendrites via improving local current density and tuning surface energy rather than mechanically by layers. It is meaningful in long-term cycling because they avoid excessive consumption of electrolyte. However, most 3D substrates, particularly Cu and non-graphitic carbon, have poor affinity for Li metal, leading to unfavorable Li deposition. To solve this issue, Cui et al. proposed a strategy of introducing lithiophilic materials to the surface of 3D frameworks, such as Au@C,30 Si@C,31 ZnO/PL,31 and ZnO/C.32–34 Nanomaterials with lower overpotential of Li anchored on a 3D conductive scaffold can provide high transfer path of ions and electrons, contributing to uniform Li nucleation and deposition. Although these efforts have been fruitful in 3D carbon materials, most of them are complicated and elaborate, and hence undesirable for practical applications. Due to its excellent conductivity and wide availability, 3D Cu current collectors have received increasing attention in this field.24,26,28,29,32,41 Most of the studies focus on preparing copper nanowires network by treating Cu foil or through chemical synthesis, which is arduous. In fact, high surface area is a double-edged sword. On the one hand, it enables smaller local current density, so as to retard the growth of dendrites.

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On the other hand, it consumes more electrolyte to form SEI, which will cause low coulombic efficiency (CE), affecting long-term cycling. In addition, the absence of lithiophilic materials makes them inferior in terms of overpotential and uniform Li entrapment. Therefore, it is promising to construct a 3D porous Cu matrix with moderate surface area and lithiophilic property by a facile method.

Previous studies have shown that by wetting molten Li on the surface, the modified graphene has smaller contact angle compared with Cu, indicating better lithiophilicity.42-44 Herein, we report a scaffold with a graphene coating on Cu foam (GN@Cu foam) as a lithiophilic host material for Li anode via a facile strategy, with improved cycling stability over a wide current density range. The as-prepared 3D current collector has a moderate surface area of 1.12 m² g⁻¹ (Fig. S1, ESI†), which reduces local current density to a degree but avoids excessive consumption of electrolyte. It is effective in alleviating Li dendrites and maintaining high CE. As displayed in Fig. 1a, under the support of graphene, Li is plated uniformly onto the framework with smooth and conformal morphology. As for the Cu foam, however, Li deposition on the skeleton is unregulated, forming Li protuberance from the substrate, irrespective of the 3D network of the host (Fig. 1b).

In half cells, GN@Cu foam demonstrates a high CE of 98.6% for 250 cycles at 0.5 mA cm⁻² and 97.4% for 150 cycles at 2 mA cm⁻². Even at a high rate of 5 mA cm⁻², the GN@Cu foam achieves a CE of 96.5% for 90 cycles. While cycling in symmetric cells, GN@Cu can deliver an areal capacity of 6 mAh cm⁻² at 6 mA cm⁻². Due to the lithiophilicity of graphene, the composite anode shows a voltage hysteresis as low as 10 mV over 2000 h in symmetric cells at 0.5 mA cm⁻². In addition, the 3D conductive structure affords space for volume changes and facilitates charge transfer during charge/discharge processes. This strategy reveals that anchoring graphene on Cu foam enables it to become a favorable host material towards a dendrite-free and stable Li anode.

Fig. 1 Schematic illustration of the Li deposition on (a) Cu foam and (b) GN@Cu foam. SEM images of (c−e) Cu foam and (f−h) GN@Cu foam, the graphene was anchored on the scaffold of Cu foam by thermal reduction.
Experimental

Preparation of GN@Cu foam

Cu foam was punched into disks with diameter of 14 mm and washed with ethanol and acetone to remove surface impurities. GO was prepared from graphite flakes by a modified Hummers method. The Cu foam was dipped in the GO solution (1 mg mL⁻¹) for 1 minute and transferred in the oven for drying at 60 °C for 2 h. GN@Cu foam was obtained after annealing under N₂ atmosphere at 300 °C for 2 h. The mass of a GN@Cu foam disc is 40 mg and the thickness is about 270 μm (Fig. S6†).

Characterizations

The BET test was performed under an Autosorb IQ Gas Sorption System at 77 K. Raman spectra were recorded with an XploRA Laser Raman spectrometer at 532 nm. The electrical conductivity of the sample films was calculated on a four-probe meter (Shanghai Qianfeng Electronic Instrument co. Limited, SB120/2) using the four probe method. SEM images were recorded on a Zeiss Ultra-55 field emission scanning electron microscope. Elemental analysis was carried out on an energy-dispersive X-ray spectroscopy system of SEM. Before SEM analysis, the GN@Cu foam-coated Li anodes were rinsed with DOL and DME solvents (1:1 by volume) to remove residual electrolyte and lithium salts and then dried in the glove box at room temperature.

Electrochemical measurements

Coin-type cells (CR2016) were assembled for all electrochemical measurements in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. The electrolyte was 1 M LiN(CF₃SO₂)₂ (LiTFSI) with 2% LiNO₃ in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 by volume ratio). A polypropylene membrane (Celgard 2400) was used as the separator. EIS was conducted over the frequency range from 100 kHz to 0.01 Hz under open circuit potential on a CHI 660E electrochemical workstation (CH Instruments Inc.). The galvanostatic discharge/charge measurements were tested at different current rates on a LAND electrochemical testing system (Land CT2001A). The charge–discharge test was operated at 25 °C.

To test the coulombic efficiency, half cells with GN@Cu foam or Cu foam as the working electrode and Li metal as the counter electrode were assembled. The amount of electrolyte used was 120 μL. The batteries were first cycled at 0–1 V (versus Li⁺/Li) at 50 μA for five cycles to stabilize the SEI layer. Then, a fixed amount of Li (1 mA h cm⁻²) was plated onto the current collector and then charged to 0.5 V (versus Li⁺/Li) to strip the Li at different current densities.

Symmetric cells were fabricated to evaluate the long-term cycling stability. 2 mA h cm⁻² (cycling test) or 7 mA h cm⁻² (rate test) of Li was first deposited on the current collectors at 0.5 mA cm⁻². Then, GN@Cu foam-coated Li electrodes were taken out from the disassembling cells in an argon-filled glove box and two of them were reassembled into symmetric batteries. The amount of electrolyte used was 40 μL. The Li foil symmetric batteries were assembled with two Li disks (Ø15 mm).

For full cells, LiFePO₄ (LFP) was employed as the cathode and GN@Cu foam Li or Li foil was used as the anode. LiFePO₄, super-P and poly-(vinyl difluoride) (8:1:1) were mixed in N-methyl pyrrolidone (NMP) to form a homogeneous slurry, and then pasted on an Al foil. The mixture was dried at 100 °C under vacuum for 12 h. The areal capacity of LFP is 3 mg cm⁻². The electrolyte was the same as that in the half and symmetric cells and the amount of electrolyte was 40 μL. The full cells were cycled between 2.5 and 4.0 V.

Results and discussion

Fig. 1c shows the scanning electron microscopy (SEM) images of bare Cu foam, which is made of an interconnecting micron copper network with diameter of ~40 μm. To obtain GN@Cu foam, the Cu foam was dipped in graphene oxide (GO) solution, followed by drying and annealing under N₂ atmosphere. As illustrated in Fig. 1h, the skeleton of the Cu foam is wrapped by a graphene layer uniformly. Fig. S1† shows that GN@Cu foam has larger specific surface area (1.12 m² g⁻¹) than that of Cu foam (0.15 m² g⁻¹), which is beneficial for lowering local current density and prolonging the initiation of Li dendrites. Raman spectrum was recorded to evaluate the graphitization degree of GN prepared by thermal reduction (Fig. S2, ESI†). There are two main peaks located at 1350 and 1600 cm⁻¹, corresponding to the D and G bands, respectively. The high value of I_D/I_G (1.25) demonstrates the high graphitization degree of GN, implying good electronic conductivity. GN@Cu foam presents a high electrical conductivity of 2 × 10⁴ S m⁻¹, which was measured by a four-probe meter. These features of GN@Cu foam render it as a firm and conductive scaffold with good mechanical strength and cycling stability. To further verify the decoration of graphene on the framework of Cu foam, energy-dispersive X-ray spectroscopy (EDS) mapping of GN@Cu foam was performed (Fig. S3†). The element distribution images of Cu and C reveals that graphene was evenly coated over the network of Cu foam, preserving a conformal morphology.

Characterization of Li plating/stripping

The morphology evolution of Li plating/stripping on Cu foam and GN@Cu foam was investigated by SEM characterization (Fig. 2). 1 mA h cm⁻² Li was plated in half cells with Li foil as the counter electrode at a current density of 0.5 mA cm⁻² and 1 M lithium bis(trifluoromethane)sulphonimide (LiTFSI) dissolved in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 1:1 by volume) with 2% LiNO₃ additive served as the electrolyte. After plating 1 mA h cm⁻² Li, as shown in Fig. 2a and b, Cu foam forms an uneven Li deposition with some aggregation and a protuberance grew from the skeleton, which was attributed to the poor lithiophilicity of Cu and the resultant irregular nucleation. In contrast, GN@Cu foam displays a uniform and smooth morphology after Li deposition on its surface (Fig. 2c and d). The homogeneous Li growth can be attributed to the lithiophilic coating of graphene, which enables the uniform...
nucleation of Li. Furthermore, GN@Cu foam with enlarged surface area contributes to low local current density, leading to favorable mass transfer resistance and nucleation/growth behavior.\(^{45-47}\) Upon stripping, Li disappears from the substrates and both the Cu foam and the GN@Cu foam recover their initial morphology with an extra layer of solid electrolyte interface (SEI) film on the surfaces (Fig. 2c–h). The Raman spectrum after 10 cycles manifests the structural integrity of GN@Cu foam (Fig. S2†). To further confirm the reversibility and cycling stability of Li plating and stripping, SEM images of Li deposited on Cu foam and GN@Cu foam were investigated (Fig. 2i–j). It can be seen that numerous Li particles and aggregates are covered on the surface of the Cu foam, indicating poor reversibility and low CE of Cu foam as a host material for the Li anode. The irregular and lumpy Li deposition has potential safety hazards and may eventually induce the growth of dendrites. On the contrary, after 100 cycles, the electrode surface of GN@Cu foam remained flat and smooth without any protruding Li. The uniform and dendrite-free Li plating on GN@Cu foam demonstrates that it is a stable host material with high reversibility of Li plating/stripping. These results highlight the importance of lithiophilic coating on the 3D current collectors for uniform and stable Li deposition.

Electrochemical performance

The Li deposition behavior has an important effect on the electrochemical performance. Galvanostatic cycling measurements were conducted in half cells with Cu foam or GN@Cu foam as the working electrode and Li foil as the counter electrode. 1 mA cm\(^{-2}\) Li was electroplated on the working electrode at 2 mA cm\(^{-2}\) and then, Li was stripped at the same current density until the cell voltage reached 0.5 V. Fig. 3a shows the voltage profiles of Li plating/stripping on Cu foam and GN@Cu foam electrodes in the first cycle. A sharp voltage drop with a nucleation overpotential of ~40 mV is recorded at the beginning of Li plating on the Cu foam, indicating poor affinity for Li.\(^ {48}\) The nucleation overpotential is defined as the gap between the voltage tip and the later stable mass-transfer-controlled overpotential.\(^ {42}\) In contrast, GN@Cu foam exhibits much smoother voltage dip at the initial stage with negligible nucleation overpotential, verifying the lithiophilic property of GN@Cu foam, which is consistent with the SEM results. Additionally, the potentials of Li plating/stripping on GN@Cu foam are ~100 mV and 100 mV, much lower than that of Cu foam (~260 mV and 260 mV). The cycling stability was evaluated via the CE of repeated discharge/charge processes. As shown in Fig. 3b, the CE of GN@Cu foam is maintained at 97.4% for nearly 150 cycles, while that of Cu foam is only 96.4% and declines after 40 cycles. The potentials of Li plating/stripping on Cu foam and GN@Cu foam in the 100\(^{th}\) cycle are shown in Fig. S7.\(^ {†}\) It can be seen that GN@Cu foam has lower hysteresis and better reversibility than those of the Cu foam. This is attributed to the graphene coating, which accommodates volume change more effectively and improves the stability of the SEI layer. Voltage profiles and cycling performances were also tested at current densities of 0.5, 1 and 5 mA cm\(^{-2}\), respectively (Fig. S4†). When cycling at 0.5 mA cm\(^{-2}\), GN@Cu foam presents nucleation overpotential of 10 mV and a CE as high as 98.6% for 250 cycles (Fig. S4a and d†). Even at a high rate of 5 mA cm\(^{-2}\), the foam achieves a CE of 96.5% for 90 cycles (Fig. S4f†). It is observed that GN@Cu foam shows superior CE and cycling stability over a wide range of current density, proving its excellent reversibility in Li plating/stripping. In addition, when the areal capacities increase to 5 mA h cm\(^{-2}\), GN@Cu foam can run for 80 cycles with an average CE as high as 98% (Fig. S8†).

The rate performance of half cells is displayed in Fig. 3c from 0.5 mA cm\(^{-2}\) to 5 mA cm\(^{-2}\) and back to 0.5 mA cm\(^{-2}\). It can be seen that Cu foam has larger overpotential than that of GN@Cu foam and suffers from severe voltage fluctuation at high current densities. Furthermore, when recovered to 0.5 mA cm\(^{-2}\), the CE of GN@Cu foam increases to 98.2%, but only 80% CE of Cu foam is retained. These results imply that GN@Cu foam can
afford high current density with better reversibility. The incorporation of graphene on Cu foam makes it a more stable conductive framework for the Li host, allowing homogeneous ion flux and charge transfer. The highly reduced overpotential and stable cycling can be confirmed by electrochemical impedance spectra (EIS) analysis (Fig. 3d). After 1 cycle of Li plating/stripping, the charge-transfer resistance ($R_{ct}$) of GN@Cu foam is 10 $\Omega$, which is smaller than that of Cu foam (18 $\Omega$), thus explaining the better rate performance of the GN@Cu foam. This also indicates that the 3D current collector is effective in decreasing the local current density. The $R_{ct}$ of GN@Cu foam is 5 $\Omega$ after 100 cycles, revealing better conductivity after cycling, which may be ascribed to residual Li. As for the Cu foam, $R_{ct}$ reduces to 5 $\Omega$ after 45 cycles, indicating that more Li is left in the working electrode after stripping, which is in agreement with the low CE of the Cu foam.

The long-cycle stability of GN@Cu foam was investigated in symmetrical cells. The electrode was first electroplated with Li onto the framework. Fig. 4a compares the voltage profiles of symmetric GN@Cu foam Li cells and the bare Li foil counterparts at 0.5 mA cm$^{-2}$ for 1 mA h cm$^{-2}$ Li. It is evident that GN@Cu foam has a more stable cycling performance than bare Li foil. The bare Li symmetric cell shows gradually increased hysteresis after 280 h due to the breakage of SEI and dendrites formation, while the GN@Cu foam Li cell exhibits a stable voltage hysteresis without fluctuation over 2000 h, indicating the uniform Li plating/stripping behavior on the GN@Cu foam. To study the evolution of voltage profiles in detail, the 1$^{st}$, 7$^{th}$, 20$^{th}$ and 400$^{th}$ cycles of the cells were magnified and shown in Fig. 4b. Clearly, the GN@Cu foam Li cell presents flat discharge/charge plateaus with much smaller voltage hysteresis (10 mV) than that of Li foil (52–100 mV). This is a significant improvement compared with the Li foil cell, resulting from the lower current density due to the enlarged surface area of the GN@Cu foam. Furthermore, graphene anchored on the Cu foam improves the stability of the SEI layer, so as to prolong the lifespan of symmetric cells. The GN@Cu foam Li cells also show superior performance compared to the Cu foil Li cells, which show increased hysteresis after 250 h (Fig. S9†). When the current density was increased to 4 mA cm$^{-2}$, stable cycling beyond 200 cycles without distinct hysteresis increase can be detected for the GN@Cu foam Li cell (Fig. S5†). However, the voltage profile of the Li foil cell shows an abrupt augment after 20 cycles. The enlarged voltage profiles of specific cycles, as shown in Fig. S5b,† confirm the stable cycling of the GN@Cu foam Li cell with smaller hysteresis (50 mV) than that of the Li foil cell (120 mV). The rate performance of symmetric cells was tested by cycling over a current density range from 0.5 mA cm$^{-2}$ to 6 mA cm$^{-2}$. The Li-plating or Li-stripping process of each cycle was 1 h. The voltage hysteresis increases with current density and remains stable during cycling at the same current density except for the fluctuant voltage response of Li foil at high current density. It can be seen that the voltage profiles change more gently in GN@Cu foam Li cells compared with Li foil cells, indicating better charge transfer within 3D current collectors. These results illustrate that GN@Cu foam Li electrodes can effectively improve cycling stability and decrease voltage hysteresis due to its favorable Li deposition and charge-transfer kinetics. Furthermore, the maximum accommodation of Li metal in GN@Cu foam can reach 10 mA h cm$^{-2}$ (Fig. S10†) and the corresponding volume capacity is 370 mA h cm$^{-3}$, which is important for its practicality.

To explore the practical application of GN@Cu foam Li electrodes, full cells with LiFePO$_4$ (LFP) as the cathode were assembled. In comparison with Li foil/LFP cells, the GN@Cu foam Li/LFP cells show smaller voltage polarization at 0.2C (Fig. 5a), benefiting from the highly conductive interconnected
framework of the GN@Cu foam. The cycling performance of full cells was tested at 0.2C and 0.5C (Fig. 5b and c). It can be seen that the difference in cycling stability is small at 0.2C but significant at 0.5C. The capacity retention was 98% after 100 cycles at 0.2C and 96% after 300 cycles at 0.5C for GN@Cu foam Li/LFP cells, compared with 95% and 77%, respectively, for Li foil/LFP cells. Fig. 5d shows the rate performance of full cells from 0.2C to 5C. Similarly, GN@Cu foam Li/LFP cell delivers almost the same capacity as the Li foil/LFP cell at low current density but has superior capacity at high rates. It displays a capacity of 158 mA h g⁻¹ at 0.2C and retains 65 mA h g⁻¹ at 5C, while the capacities of the cell with Li foil are 158 mA h g⁻¹ and 22 mA h g⁻¹ at 0.2C and 5C, respectively. The performance of Cu foil Li/LFP full cells is shown in Fig S11,† which shows larger voltage polarization and retains 84% of its initial capacity after 100 cycles. Therefore, GN@Cu foam Li electrodes show advantages over Li foil in full cells in terms of cycling stability and rate performance, indicating their great potential for practical application.

Conclusions

In summary, we have developed a facile approach to prepare a 3D current collector with lithiophilic property by coating graphene on Cu foam as the host material for an advanced Li anode. The 3D structure of the scaffold with graphene helps in accommodating volume changes and stabilizing the SEI film, which contributes to the stable cycling performance. In addition, the enlarged surface area effectively decreases the local current density and as a result, narrows the overpotential and alleviates dendritic formation. Furthermore, the high conductivity and lithiophilicity of graphene facilitates charge transfer and ion flux, inducing uniform Li nucleation and deposition. Consequently, the GN@Cu foam exhibits excellent cycling performance over a wide current density range in both half and symmetric cells and shows practical potential in full cells. This study provides a novel and feasible strategy to modify Cu foam, making it possible to produce a stable and dendrite-free Li anode, which opens up new opportunities for fabricating 3D current collectors with lithiophilic property and promotes the realization of high-energy-density systems.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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