DOI: 10.1002/((please add manuscript number))

Article type: Communication

Graphitic Carbon Nitride induced Micro Electric Field for Dendrite-Free Lithium Metal Anodes

Ziyang Lu[†], Qinghua Liang[†], Bo Wang, Ying Tao, Yufeng Zhao, Wei Lv, Donghai Liu, Chen Zhang, Zhe Weng, Jiachen Liang, Huan Li, and Quan-Hong Yang**

Z. Lu, Y. Tao, D. Liu, C. Zhang, Z. Weng, J. Liang, H. Li, and Prof. Q.-H. Yang

Nanoyang Group, State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University Tianjin 300350, China
E-mail: qhyangcn@tju.edu.cn

Q. Liang and Prof. W. Lv
Shenzhen Geim Graphene Center, Graduate School at Shenzhen,
Tsinghua University, Shenzhen 518055, China
E-mail: lv.wei@sz.tsinghua.edu.cn

B. Wang and Prof. Y. Zhao
Key Laboratory of Applied Chemistry, Yanshan University,
Qinhuangdao 066004, China

[†]These authors contribute equally to this work.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/aenm.201803186](https://doi.org/10.1002/aenm.201803186).

This article is protected by copyright. All rights reserved.

Keywords: lithium metal anodes, graphitic carbon nitride (g-C₃N₄), nucleation, dendrites, micro electric field

Uncontrolled dendrites resulting from non-uniform lithium (Li) nucleation/growth and Li volume expansion during charging cause serious safety problems for Li anode-based batteries. Here we report the coating of nickel foam with graphitic carbon nitride (g-C₃N₄) to have a three-dimensional (3D) current collector (g-C₃N₄@Ni foam) for dendrite-free Li metal anodes. The lithiophilic g-C₃N₄ coupled with the 3D framework is demonstrated to be highly effective for promoting the uniform deposition of Li and suppressing the formation of dendrites. Both DFT calculations and experimental studies indicate the formation of a micro electric field (MEF) resulting from the tri-s-triazine units of g-C₃N₄, which induce numerous Li nuclei during the initial nucleation stage, effectively guiding the following Li growth on the 3D Ni foam to be well-distributed. Furthermore, the 3D porous framework is favorable for absorbing any volume change and stabilizing the solid electrolyte interphase (SEI) layer during repeated Li plating/stripping. As such, a Li metal anode based on the g-C₃N₄@Ni foam has a remarkable electrochemical performance with a high Coulombic efficiency (98% retention after 300 cycles), an ultralong lifespan up to 900 hours as well as a low overpotential (< 15 mV at 1.0 mA cm⁻²) at a Li deposition of 9.0 mAh cm⁻².

Due to its advantages of light weight (0.53 g cm⁻³), high theoretical specific capacity (3860 mAh g⁻¹), and low redox potential (-3.04 V *vs* RHE),^[1-5] Li metal is widely deemed to be an ideal anode for many promising batteries such as Li-S,^[6-7] Li-Se,^[8] Li-O₂^[9] that have extremely high energy densities. However, the non-uniform deposition of Li ions (Li⁺) and the large volume change of the Li-metal anode during cycling results in the formation of numerous cracks in the solid-electrolyte interface (SEI) layers,^[10-12] which accelerate the inhomogeneous deposition of Li and consume more electrolyte,^[12, 13] causing significant safety issues and low Coulombic efficiency (CE).^[14-16] In order to solve these problems, tremendous efforts have been made to achieve uniform Li deposition or a steady SEI passivation layer by modifying the solid-state electrolyte,^[3, 17-19] using lithiophilic hosts,^[20-24] and adding electrolyte additives.^[25-27] Another critical issue is the effect of current density on Li deposition behavior.^[28-29] Compared with planar electrodes, a 3D current collector effectively reduces the local current density and delays Li dendrite growth rate due to a larger specific surface area.^[30-34] However, there is a large nucleation overpotential for Li deposition on most of the common metal current collectors even with a 3D structure (Ni, Cu, Al).^[35] The sporadic nucleation caused by the large nucleation overpotential during the initial stage directly leads to non-uniform Li deposition in the following growth stage.^[36-39] Thus, these 3D foams do not intrinsically realize uniform Li deposition.^[22] As is well known, the Li nucleation behavior depends on the Li plating substrate.^[37-40] For example, both theoretical calculations and experiment results show that N-doped graphene is lithiophilic and helps achieve uniform Li nucleation due to the strong binding of N species (pyridinic and pyrrolic nitrogen) with Li⁺.^[36] In another example, the ultrafine silver (Ag) nanoparticles as the seeds has been reported to direct the deposition of Li within the 3D host materials.^[37] The initially formed Li nucleating layer then serves as seeds to regulate uniform Li growth.^[10, 35, 38] However, the extremely

low N-doping amount has a limited effect on the uniform nucleation of Li, and the complex process of modifying the substrate severely limits its practical application. The uniform deposition of Li can be achieved by adjusting the local electric field which has a significant influence on the deposition behavior of Li^+ in the electrochemical process.^[14, 41] Therefore, developing a 3D current collector with a lithiophilic surface coupled with a pre-designed micro-electric field could achieve initial homogenous Li nucleation followed by uniform deposition, effectively reducing the local current density and suppressing the volume expansion.

Following this idea, we here propose a dendrite-free Li metal anode that uses 3D Ni foam uniformly coated with graphitic carbon nitride ($\text{g-C}_3\text{N}_4$ @Ni foam) as the current collector (**Figure 1**). The naturally-formed ring-shaped micro electric field (MEF) induced by the six p-electrons of the N atoms at the tri-s-triazine units of $\text{g-C}_3\text{N}_4$ not only gives $\text{g-C}_3\text{N}_4$ a better Li affinity (See density functional theory (DFT) calculation below) that induces more Li nucleation sites but also significantly lowers the Li nucleation overpotential compared with that of pure Ni foam. Electrochemical tests reveal that the $\text{g-C}_3\text{N}_4$ @Ni foam provides numerous nucleation sites that promote uniform and smooth Li deposition and growth. As such, a stable CE of 98% for 300 cycles was achieved at a current density of 0.5 mA cm^{-2} with an areal capacity of 1.0 mA h cm^{-2} . Remarkably, symmetrical cell tests using the $\text{Li@g-C}_3\text{N}_4$ @Ni foam show a very small polarization with an ultra-long lifespan of over 900 h at 1.0 mA cm^{-2} . In addition, the $\text{Li@g-C}_3\text{N}_4$ @Ni foam| LiCoO_2 full cells show excellent stability at 1.0 C (72.9% retention after 200 cycles). $\text{Li@g-C}_3\text{N}_4$ @Ni foam|S cells also show an outstanding capacity retention rate at 1.0 C (65.6% after 500 cycles), which is superior to Li@Ni foam|S cells (51.8% after 500 cycles).

N doping is considered to be effective in increasing the lithiophilicity of carbon materials.^[36] The $\text{g-C}_3\text{N}_4$ has a N content of 57 at% and is believed to have a remarkable affinity with Li^+ . Therefore, DFT calculations were carried out to study the interaction between Li^+ and $\text{g-C}_3\text{N}_4$ as well as the nucleation behavior of Li on $\text{g-C}_3\text{N}_4$. Seven structures for Li^+ absorbed on $\text{g-C}_3\text{N}_4$ were constructed and optimized (**Figure S1**) and the same stable adsorption structure was obtained

after optimization (**Figure 2a**). This configuration has the highest binding energy with Li^+ , and is consistent with previous reports.^[42-43] This result can be explained by an analysis of the charge transfer on $\text{g-C}_3\text{N}_4$ (**Figure 2b**). The N of $\text{g-C}_3\text{N}_4$ has a pair of p -electrons and the electronegativity of N ($\chi = 3.04$) is much larger than C ($\chi = 2.55$). It is found that the six negatively charged N atoms of the tri-s-triazine units can locally form a strong ring-shaped negative micro electric region (MEF marked in yellow), resulting in a MEF directed towards the negatively charged N centers. Such a MEF is favorable for capturing the positively charged Li^+ during Li-plating to form a relatively stable structure (**Figure 2b**). This is similar to the strong adhesion between Lewis base sites (N) and Lewis acidic Li^+ (light blue) in electrolytes.^[44] Thus, the $\text{g-C}_3\text{N}_4$ has a large binding energy of -3.75 eV with Li^+ , suggesting a strong interaction between Li^+ and $\text{g-C}_3\text{N}_4$. In contrast, Ni has a much smaller binding energy of -1.25 eV (**Figure 2c**) compared with $\text{g-C}_3\text{N}_4$. In addition, the binding energy of Cu with Li^+ is also smaller than that of $\text{g-C}_3\text{N}_4$ according to previous literature reports.^[36] Due to the strong interaction between $\text{g-C}_3\text{N}_4$ and Li^+ , Li^+ are more likely to adsorb on $\text{g-C}_3\text{N}_4$. As such, the $\text{g-C}_3\text{N}_4$ induces uniform Li nucleation on the surface of the anode. Furthermore, high content of N species of $\text{g-C}_3\text{N}_4$ provides a large number of nucleation sites with a low overpotential so that the $\text{g-C}_3\text{N}_4$ is expected to produce numerous nucleation sites and a smaller nucleation overpotential.

Figure 1. Schematic of the Li nucleation and plating process on Ni foam and g-C₃N₄@Ni foam.

Experimentally, the 2D g-C₃N₄ nanosheets (**Figure 2d** and **Figure S2**) are prepared by thermal polymerization and can be easily coated on Ni foam (g-C₃N₄@ Ni foam) by a multiple impregnation method (**Figure 2e**). After coating with the g-C₃N₄ nanosheets, the Ni foam retains its 3D structure with no accumulation of g-C₃N₄ on the top surface. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to investigate the crystal structure and the bonding structure of the g-C₃N₄ nanosheets on Ni foam. The XRD pattern of g-C₃N₄ showed two distinct diffraction peaks at around 13.2° and 27.3° (**Figure 2f**), which correspond to the (100) and (002) planes, respectively.^[45] The FTIR spectrum confirms the bonding structure of g-C₃N₄ (**Figure S3**), as reflected by characteristic bands at 1200-1600 cm⁻¹ (skeletal vibrations of CN heterocycles) and 810 cm⁻¹ (breathing vibration of triazine units). Two small

peaks between 3000 and 3500 cm^{-1} suggest the exposure of surface amino (N-H) groups in g- C_3N_4 on the Ni foam.^[46] X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition of g- C_3N_4 on the surface of the Ni foam. **Figure 2g** shows the high-resolution C1s spectrum of g- C_3N_4 , which can be deconvoluted into three C species. The peak at 284.8 eV originates from adventitious carbon (sp^3 C-C), while the other two components at 286.2 (C-N) and 288.0 eV (N=C-N) are ascribed to two different carbon species in the basic aromatic CN heterocycles. The N 1s spectra can also be fitted by three peaks located at 401.0, 399.0, and 398.5 eV (**Figure 2h**), which are respectively due to N atoms in surface amino groups, tri-coordinated N atoms, and di-coordinated N atoms (C-N=C) in the aromatic CN heterocycles.^[46] The relatively high specific surface area of g- C_3N_4 is also beneficial for the uniform deposition of Li^+ (**Figure S4**). The energy dispersive X-ray spectroscopy (EDX) maps (**Figure S5**) reveal the homogeneous distribution of C and N in the Ni foam framework, demonstrating that g- C_3N_4 has been uniformly coated on the surface of the Ni foam. Furthermore, from the optical micrographs at different magnifications (**Figure S6**), we can see that the surface of the Ni foam skeleton has a unique metallic lustre. After modification by the g- C_3N_4 , this lustre disappears and the surface becomes pale yellow, indicating the successful coating of the Ni foam by g- C_3N_4 .

The existence of a MEF on the Ni foam caused by g- C_3N_4 was experimentally verified by the significantly reduced nucleation overpotential. The nucleation overpotentials of Li plating on Cu foil, Ni foam and g- C_3N_4 @Ni foam electrodes were studied at current densities ranging from 0.1 to 1.0 mA cm^{-2} (**Figure 2i** and **Figure S7**). The nucleation overpotential on the g- C_3N_4 @Ni foam electrode was 11 mV at 0.1 mA cm^{-2} and increased to 33 mV when the current density increased to 1.0 mA cm^{-2} . These values are much lower than that of a Ni foam electrode (56 mV at 1.0 mA cm^{-2}) and a Cu foil (110 mV at 1.0 mA cm^{-2}). With higher current density (**Figure S7**), the

nucleation overpotential of the g-C₃N₄@Ni foam electrode is still much lower than that of a Ni foam electrode (96 mV at 5.0 mA cm⁻²) and a Cu foil (174 mV at 5.0 mA cm⁻²). A significantly reduced nucleation overpotential also demonstrates the strong ability of the MEF to capture Li⁺. The XRD and FTIR spectrum collected after lithiation reveal the almost unchanged structure of g-C₃N₄ after Li deposition (**Figure S8**).^[47] The disappearance of the (100) peak in the XRD pattern after Li deposition indicates that the deposition occurs at the tri-s-triazine units. Due to the large number of lithiophilic N species in g-C₃N₄, the g-C₃N₄@Ni foam shows a much lower electrical resistance than the pure Ni foam. This is confirmed by the Nyquist plots for cells with Ni foam and g-C₃N₄@Ni foam electrodes (**Figure S9**). In both case for the first run and after ten cycles the Li@g-C₃N₄@Ni foam show a smaller interface impedance than Ni foam electrodes.

Figure 2. (a) Crystal models for calculating the binding energy of a Li^+ adsorbed on $\text{g-C}_3\text{N}_4$ and (b) the corresponding charge density difference (brown, purple and green balls represent carbon atoms, nitrogen atoms and Li atoms, respectively, yellow and light blue areas represent positive and negative charge differences). (c) Crystal models for calculating the binding energy of a Li^+ adsorbed on Ni (blue and green balls represent nickel atoms and Li atoms, respectively). (d) High-resolution transmission electron microscope (HR-TEM) image of the $\text{g-C}_3\text{N}_4$. (e) SEM image of the $\text{g-C}_3\text{N}_4@\text{Ni}$ foam. (f) XRD pattern of the $\text{g-C}_3\text{N}_4$. (g) C 1s XPS spectra and (h) N 1s XPS spectra of the $\text{g-C}_3\text{N}_4$. (i) Li nucleation overpotentials on $\text{g-C}_3\text{N}_4@\text{Ni}$ foam, Ni foam, and Cu electrodes at different current densities. The nucleation overpotential is defined as the

difference between the sharp tip voltage and the later stable mass transfer-controlled overpotential.

By using Li metal as the counter electrode, the deposition process was studied for the g-C₃N₄@Ni foam and Ni foam at a current density of 1.0 mA cm⁻². The SEM images of different amounts of Li deposition were recorded (**Figures 3a-h**). It was found that no Li dendrites was formed when Li was gradually plated on the g-C₃N₄@Ni foam. Furthermore, no obvious Li was observed on the outside surface of the g-C₃N₄@Ni foam even after deposition of Li for 1.0 (**Figure S10**) and 3.0 mAh cm⁻² (**Figure 3a-c**), indicating the uniform deposition of Li inside the 3D framework. The g-C₃N₄ would be covered when a certain amount of Li was deposited, and the g-C₃N₄ would not directly affect the subsequent lithium deposition. However, it should be emphasized that the as-produced numerous Li nuclei during the initial nucleation stage directly guides the following Li deposition process. This was validated by the even deposition with a relatively high amount of lithium (**Figure 3d-h**). After further deposition of more Li (5.0 mAh cm⁻²), the 3D skeleton was still maintained with no discernible dendrites (**Figures 3d-f**). When the amount of Li deposition reached 9.0 mAh cm⁻², the 3D framework of the Ni foam was also maintained (**Figures 3g-h**). The uniform Li deposition on the framework is explained by the diagram in **Figure 3i**. In contrast, on a pure Ni foam significant uneven deposition occurred after deposition of Li for 5.0 mAh cm⁻² (**Figure S11**). The pores in the Ni foam were completely blocked and the skeletal structure of the foam was barely discernible when the Li deposition reached 9.0 mAh cm⁻² (**Figure 3j-l**). This is consistent with the above DFT calculations and previous assumption and confirms that the MEF of g-C₃N₄ effectively promotes uniform nucleation, with the homogeneously distributed nucleation sites well guiding the Li deposition. Due to the uniform deposition of Li induced by the MEF, the local current density is spread over

a large area and never becomes excessively large, so that the formation of Li dendrites is effectively suppressed.

Figure 3. (a) SEM image of the g-C₃N₄@Ni foam after plating with 3.0 mA h cm⁻² Li and magnified SEM images (b-c). (d) SEM image of the g-C₃N₄@Ni foam after plating with 5.0 mA h cm⁻² Li and magnified SEM images (e-f). (g) SEM image of the g-C₃N₄@Ni foam after plating with 9.0 mA h cm⁻² Li and a magnified SEM image (h). (i) Diagram after plating with 9.0 mA h cm⁻² Li

on g-C₃N₄@Ni foam. (j) SEM image of the Ni foam after plating with 9.0 mA h cm⁻² Li and a magnified SEM image (k). (l) Diagram after plating with 9.0 mA h cm⁻² Li on Ni foam.

The uniform nucleation and deposition of Li on g-C₃N₄@Ni foam improves the CE of the Li anodes. As shown in **Figure 4a**, the g-C₃N₄@Ni shows a stable CE of 98% after 300 cycles with a current density of 0.5 mA cm⁻² and an areal capacity of 1.0 mA h cm⁻². By comparison, the Cu foil and Ni foam show a rapidly decreasing CE. With a higher current density and deposition capacity (1.0 mA cm⁻² with 2.0 mA h cm⁻²), the g-C₃N₄@Ni foam CE stabilizes at 97% after 140 cycles (**Figure 4b**), but those of Cu foil and Ni foam show rapid drop within 80 cycles. The much higher CE of g-C₃N₄@Ni than the Cu foil and Ni foam prove that uniform Li nucleation, deposition, and a reduced local current density are effective for stabilizing the SEI. As shown in **Figure 4c**, it is seen that the g-C₃N₄@Ni foam shows excellent plating/stripping stability with little voltage hysteresis except during the first few cycles. That is attributed to the formation of the SEI layer in the first cycle and essential for stabilizing subsequent cycles. The g-C₃N₄@Ni foam also shows excellent stability under a high current density and high areal capacity test conditions (3.0 mA cm⁻² and 8.0 mA h cm⁻²). As shown in **Figure 4d**, the g-C₃N₄@Ni foam shows excellent stability in the plating/stripping with a small voltage hysteresis after 40 cycles. In order to further verify that the g-C₃N₄@Ni foam promotes uniform nucleation and deposition, symmetrical cells were assembled for testing. As shown in **Figure 4e**, even at a high Li deposition amount of 9.0 mA h cm⁻², a symmetrical cell based on Li@g-C₃N₄@Ni foam shows a relatively low and stable overpotential (<15 mV) with good cycling stability for more than 900 h. In contrast, a symmetrical cell based on Li@Ni foam shows obvious voltage fluctuations and an increasing overpotential as the test time increases. The Li@Cu-based symmetrical cell exhibits an overpotential of more than 40 mV after 210 h. In order to study the voltage changes

during the deposition/dissolution process, the 130-140 h and 600-610 h intervals were examined in more details (**Figure 4f**). The Li@g-C₃N₄@Ni foam-based symmetrical cell shows a smaller overpotential and more stable voltage polarization than both the Li@Ni foam-based and Li@Cu-based symmetrical cells. Furthermore, under a larger current density of 2.0 mA cm⁻² (**Figures 4g and S12**), the Li@g-C₃N₄@Ni foam-based symmetrical cell still shows a small overpotential of ~20 mV for experiments lasting more than 500 h. As can be seen from the SEM image of Li@Ni and Li@g-C₃N₄@Ni foams after 200 cycles of plating/stripping tests, Li dendrites appear on the surface of the Li@Ni foam (**Figure S13**), while there is almost no dendrite formation on the Li@g-C₃N₄@Ni foam and its 3D pore skeleton structure is well maintained (**Figure S14**). These results confirm that the uniform deposition of Li on g-C₃N₄@Ni foam facilitates the formation of a uniform SEI layer, thereby improving the charge transfer kinetics. The interfacial stability of the SEI was further studied by electrochemical impedance spectroscopy (EIS). As shown in **Figure S15**, in both cases for initial condition and after 10 cycles of Li plating/stripping, the Li@g-C₃N₄@Ni foam-based symmetrical cells show a smaller semicircle than the Li@Ni foam-based cell in the high frequency range. This indicates that Li@g-C₃N₄@Ni foam has a smaller interface impedance of its SEI and a smaller charge-transfer resistance at the Li metal surface than the Li@Ni foam.

Figure 4. Comparison of CE of Li plating on/stripping from $\text{g-C}_3\text{N}_4@\text{Ni}$ foam, Ni foam, and Cu electrodes with an areal capacity of (a) 1.0 mA h cm^{-2} and (b) 2.0 mA h cm^{-2} at the same current density of 2.0 mA cm^{-2} . Typical galvanostatic discharge-charge profiles of the $\text{g-C}_3\text{N}_4@\text{Ni}$ foam electrode at (c) 1.0 mA cm^{-2} for 1.0 mA h cm^{-2} and (d) 3.0 mA cm^{-2} for 8.0 mA h cm^{-2} . (e) Voltage-time profiles of Li plating/stripping with a cycling capacity of 1.0 mAh cm^{-2} at 1.0 mA cm^{-2} in a symmetrical cell. (f) Magnified Li plating/stripping profiles during the 130-140 hour and 600-610 hour periods. (g) Voltage-time profiles of the Li plating/stripping process with a cycling capacity of 1.0 mAh cm^{-2} at 2.0 mA cm^{-2} in a symmetrical cell.

To verify the superiority of the Li@g-C₃N₄@Ni foam electrodes, Li@g-C₃N₄@Ni foam and Li@Ni foam electrodes (9.0 mAh cm⁻² deposition of Li) were paired with LiCoO₂ (Structure information shown in **Figure S16**) to investigate the full-cell performance. As shown in **Figure 5a**, the Li@g-C₃N₄@Ni foam|LiCoO₂ cell has a higher and more stable capacity than the Li@Ni foam|LiCoO₂ cell at all current densities examined. In addition, the Li@g-C₃N₄@Ni foam|LiCoO₂ battery has a capacity retention of 72.9% at a rate of 1.0 C after 200 cycles, as shown in **Figure 5b**. By contrast, the capacity retention of the Li@Ni foam|LiCoO₂ cell drops to 52.8%. Using the Li@g-C₃N₄@Ni foams deposited with a small amount of Li (1 and 2 mAh cm⁻²) as the anode, the full-cells with LiCoO₂ cathodes still work well and exhibit no obvious differences (**Figures S17**). To further demonstrate the potential of the g-C₃N₄@Ni foam for practical use, the Li@g-C₃N₄@Ni foam anode was investigated in Li-S batteries that are considered to be the most promising rechargeable batteries. As expected, the Li@g-C₃N₄@Ni foam|S cells show slightly high initial capacities of 1317, 882, and 761 mAh g⁻¹ than the Li@Ni foam|S cells with values of 1286, 863, and 738 mAh g⁻¹ at current densities of 0.2, 0.5, and 1.0 C (1.0 C = 1675 mA g⁻¹), respectively (**Figure 5c**). However, the Li@g-C₃N₄@Ni foam|S cells show much higher capacity retention of 65.6% than the Li@Ni foam|S cells (51.8%) after 500 cycles at 1.0 C (**Figures 5d and S18**). The excellent cycle stability of the Li@g-C₃N₄@Ni foam|LiCoO₂ battery and Li@g-C₃N₄@Ni foam|S battery are attributed to the uniform nucleation and deposition of Li and good structural stability of 3D g-C₃N₄@Ni foam. Although the introduction of Ni foam will inevitably decrease the capacity and the energy density of the battery, the ability of hosting high amount Li while suppressing the dendrite growth makes the g-C₃N₄@Ni foam still have great potential in practical applications.

Figure 5. (a) Rate performance of Li@g-C₃N₄@Ni foam|LiCoO₂ and Li@Ni foam|LiCoO₂ cells. (b) Discharge capacity and CE of Li@g-C₃N₄@Ni foam|LiCoO₂ and Li@Ni foam|LiCoO₂ cells at 1.0 C. (c) Rate performance of Li@g-C₃N₄@Ni foam|S and Li@Ni foam|S cells (1.0 C = 1675 mA g⁻¹ for a sulfur cathode). (d) Discharge capacity and CE of Li@g-C₃N₄@Ni foam|S and Li@Ni foam|S cells at 1.0 C.

In conclusion, we have achieved the uniform nucleation and deposition of Li on 3D Ni foam collector with g-C₃N₄ coating (g-C₃N₄@Ni foam). The DFT calculation demonstrates that the inherently strong ring-shaped negative micro electric field (MEF) at the tri-s-triazine units of the g-C₃N₄ has a strong ability to capture Li⁺, thereby significantly reducing the Li nucleation overpotential. Furthermore, the uniformly distributed MEF caused by the high N content induces numerous well-distributed Li nucleation sites, thus promoting the formation of numerous Li nuclei. These in-situ formed Li nuclei guide the uniform deposition of Li. Furthermore, the 3D g-C₃N₄@Ni foam with a large specific surface area can effectively reduce

current density, thereby inhibiting the growth of Li dendrites and reducing the volume change during charge and discharge. As such, the Li@g-C₃N₄@Ni foam anode is dendrite-free, and has a high Coulombic efficiency (98%) and an ultralong lifespan (900 h) with a high Li deposition capacity of 9 mAh cm⁻². Remarkably, the Li@g-C₃N₄@Ni foam-based full batteries show excellent stability, and is obviously superior to the batteries without the g-C₃N₄ coating. Overall, this work shows a simple but effective surface modification strategy to achieve uniform metal anode deposition. More importantly, the introduction of micro electric field on electrode surface can also be extended into other electrochemical applications to improve the surface activity, such as electro-catalysis and the other energy storage devices.

Supporting Information

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

Acknowledgements

We appreciate support from the National Science Fund for Distinguished Young Scholars, China (No.51525204), the National Natural Science Foundation of China (No. 51702229 and U1601206), Guangdong Natural Science Funds for Distinguished Young Scholars (2017B030306006), the Guangdong Special Support Program (2017TQ04C664) and the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01N111).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

This article is protected by copyright. All rights reserved.

References

- [1] E. Cha, M. D. Patel, J. Park, J. Hwang, V. Prasad, K. Cho, W. Choi, *Nat. Nanotechnol.* **2018**, *13*, 337.
- [2] D. Lin, Y. Liu, Y. Cui, *Nat. Nanotechnol.* **2017**, *12*, 194.
- [3] X. Han, Y. Gong, K. K. Fu, X. He, G. T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, *Nat. Mater.* **2017**, *16*, 572.
- [4] D. S. Su, S. Perathoner, G. Centi, *Chem. Rev.* **2013**, *113*, 5782.
- [5] B. Li, Y. Wang, S. Yang, *Adv. Energy Mater.* **2018**, *8*, 1702296.
- [6] X. Ji, K. T. Lee, L. F. Nazar, *Nat. Mater.* **2009**, *8*, 500.
- [7] G. Li, Z. Chen, J. Lu, *Chem* **2018**, *4*, 3.
- [8] C. M. Park, J. H. Kim, K. H. K. Hansu, H. J. Sohn, *Chem. Soc. Rev.* **2010**, *39*, 3115.
- [9] X. Gao, Y. Chen, L. Johnson, P. G. Bruce, *Nat. Mater.* **2016**, *15*, 882.
- [10] A. Pei, G. Zheng, F. Shi, Y. Li, Y. Cui, *Nano Lett.* **2017**, *17*, 1132.
- [11] B. Liu, J. G. Zhang, W. Xu, *Joule* **2018**, *2*, 833.
- [12] M. D. Tikekar, S. Choudhury, Z. Tu, L. A. Archer, *Nat. Energy* **2016**, *1*, 16114.
- [13] D. Wang, W. Zhang, W. Zheng, X. Cui, T. Rojo, Q. Zhang, *Adv. Sci.* **2017**, *4*, 1600168.
- [14] C. P. Yang, Y. X. Yin, S. F. Zhang, N. W. Li, Y. G. Guo, *Nat. Commun.* **2015**, *6*, 8058.

- [15] H. Zhang, G. G. Eshetu, X. Judez, C. Li, M. Armand, *Angew. Chem., Int. Ed.* 2018. DOI: 10.1002/anie.201712702
- [16] X. B. Cheng, R. Zhang, C. Z. Zhao, Q. Zhang, *Chem. Rev.* **2017**, *117*, 10403.
- [17] W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram, J. B. Goodenough, *J. Am. Chem. Soc.* **2016**, *138*, 9385.
- [18] Q. Lu, Y. B. He, Q. Yu, B. Li, Y. V. Kaneti, Y. Yao, F. Kang, Q. H. Yang, *Adv. Mater.* **2017**, *29*, 1604460.
- [19] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, *Nat. Mater.* **2011**, *10*, 682.
- [20] Q. Li, S. Zhu, Y. Lu, *Adv. Funct. Mater.* **2017**, *27*, 1606422.
- [21] C. Zhang, W. Lv, G. Zhou, Z. Huang, Y. Zhang, R. Lyu, H. Wu, Q. Yun, F. Kang, Q. H. Yang, *Adv. Energy Mater.* **2018**, *8*, 1703404.
- [22] Q. Yun, Y. B. He, W. Lv, Y. Zhao, B. Li, F. Kang, Q. H. Yang, *Adv. Mater.* **2016**, *28*, 6932.
- [23] L. L. Lu, J. Ge, J. N. Yang, S. M. Chen, H. B. Yao, F. Zhou, S. H. Yu, *Nano Lett.* **2016**, *16*, 4431.
- [24] C. Zhang, Z. Huang, W. Lv, Q. Yun, F. Kang, Q-H. Yang, *Carbon* **2017**, *123*, 744.
- [25] Q. Pang, X. Liang, A. Shyamsunder, L. F. Nazar, *Nat. Energy* **2017**, *1*, 871.
- [26] X. Q. Zhang, X. B. Cheng, X. Chen, C. Yan, Q. Zhang, *Adv. Funct. Mater.* **2017**, *27*, 1605989.
- [27] W. Li, H. Yao, K. Yan, G. Zheng, Z. Liang, Y. M. Chiang, Y. Cui, *Nat. Commun.* **2015**, *6*, 7436.

- [28] C. Brissot, M. Rosso, J. N. Chazalviel, P. Baudry, S. Lascaud, *Electrochem. Acta* **1998**, *43*, 1569.
- [29] C. Brissot, M. Rosso, J. N. Chazalviel, S. Lascaud, *Stud. Surf. Sci. Catal.* **2001**, *132*, 947.
- [30] Z. Liang, D. Lin, J. Zhao, Z. Lu, Y. Liu, C. Liu, Y. Lu, H. Wang, K. Yan, X. Tao, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 2862.
- [31] A. R. O. Raji, R. V. Salvatierra, N. D. Kim, X. Fan, Y. Li, G. A. L. Silva, J. Sha, J. M. Tour, *ACS Nano* **2017**, *11*, 6362.
- [32] Y. Xu, A. S. Menon, P. P. R. M. L. Harks, D. C. Hermes, L. A. Haverkate, S. Unnikrishnan, F. M. Mulder, *Energy Storage Mater.* **2018**, *12*, 69.
- [33] R. Zhang, X. B. Cheng, C. Z. Zhao, H. J. Peng, J. L. Shi, J. Q. Huang, J. Wang, F. Wei, Q. Zhang, *Adv. Mater.* **2016**, *28*, 2155.
- [34] D. Lin, J. Zhao, J. Sun, H. Yao, Y. Liu, K. Yan, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 4613.
- [35] K. Yan, Z. Lu, H. W. Lee, F. Xiong, P. C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, *Nat. Energy* **2016**, *1*, 16010.
- [36] R. Zhang, X. R. Chen, X. Chen, X. B. Cheng, X. Q. Zhang, C. Yan, Q. Zhang, *Angew. Chem.* **2017**, *129*, 7872.
- [37] C. Yang, Y. Yao, S. He, H. Xie, E. Hitz, L. Hu, *Adv. Mater.* **2017**, *29*, 1702714.
- [38] L. Liu, Y. X. Yin, J. Y. Li, S. H. Wang, Y. G. Guo, L. J. Wan, *Adv. Mater.* **2018**, *30*, 1706216.

- [39] L. Fan, H. L. Zhuang, W. Zhang, Y. Fu, Z. Liao, Y. Lu, *Adv. Energy Mater.* **2018**, 8, 1703360.
- [40] H. Ye, S. Xin, Y. X. Yin, Y. G. Guo, *Adv. Energy Mater.* **2017**, 7, 1700530.
- [41] P. Zou, Y. Wang, S. W. Chiang, X. Wang, F. Kang, C. Yang, *Nat. Commun.* **2018**, 9, 464.
- [42] M. Hankel, D. Ye, L. Wang, D. J. Searles, *J. Phys. Chem. C* **2015**, 119, 150910111826005.
- [43] M. Wu, Q. Wang, Q. Sun, P. Jena, *J. Phys. Chem. C* **2013**, 117, 6055.
- [44] Q. Pang, X. Liang, C. Y. Kwok, J. Kulisch, L. F. Nazar, *Adv. Energy Mater.* **2016**, 7, 1601630.
- [45] P. Yang, H. Ou, Y. Fang, X. Wang, *Angew. Chem. Int., Ed. Engl.* **2017**, 56, 3992.
- [46] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You, J. Yu, *Small* **2017**, 13, 1603938.
- [47] G. M. Veith, L. Baggetto, L. A. Adamczyk, B. Guo, S. S. Brown, X. G. Sun, A. A. Albert, J. R. Humble, C. E. Barnes, M. J. Bojdys, *Chem. Mater.* **2013**, 25, 503.

g-C₃N₄-coated nickel foam is demonstrated to be highly effective for promoting uniform lithium deposition. The unique micro electric field at the tri-s-triazine units of g-C₃N₄ induces numerous Li nuclei at initial nucleation stage and subsequently, these Li nuclei guide well-distributed Li plating on 3D Ni foam.

lithium metal anodes, graphitic carbon nitride (g-C₃N₄), nucleation, dendrites, micro electric field

Ziyang Lu[†], Qinghua Liang[†], Bo Wang, Ying Tao, Yufeng Zhao, Wei Lv*, Donghai Liu, Chen Zhang, Zhe Weng, Jiachen Liang, Huan Li, and Quan-Hong Yang*

Graphitic Carbon Nitride induced Micro Electric Field for Dendrite-Free Lithium Metal Anodes

Author Manuscript

This article is protected by copyright. All rights reserved.

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Lu, Z.;Liang, Q.;Wang, B.;Tao, Y.;Zhao, Y.;Lv, W.;Liu, D.;Zhang, C.;Weng, Z.;Liang, J.;Li, H.;Yang, Q-H

Title:

Graphitic Carbon Nitride Induced Micro-Electric Field for Dendrite-Free Lithium Metal Anodes

Date:

2019-02-14

Citation:

Lu, Z., Liang, Q., Wang, B., Tao, Y., Zhao, Y., Lv, W., Liu, D., Zhang, C., Weng, Z., Liang, J., Li, H. & Yang, Q. -H. (2019). Graphitic Carbon Nitride Induced Micro-Electric Field for Dendrite-Free Lithium Metal Anodes. *Advanced Energy Materials*, 9 (7), <https://doi.org/10.1002/aenm.201803186>.

Persistent Link:

<http://hdl.handle.net/11343/285274>