Horizontal Centripetal Plating in the Patterned Voids of Li/Graphene Composites for Stable Lithium-Metal Anodes

The dendrite problem is fundamentally suppressed by horizontal centripetal plating of Li in the patterned voids of reduced graphene oxide/Li composite anodes. The mitigated thickness fluctuation and homogeneous Li\(^+\) distribution enable high performance in both half and full cells. The patterned composite anodes are promising for developing high-energy-density Li-metal batteries.

**HIGHLIGHTS**

- Periodic patterned anodes of alternately layered Li and graphene composite are constructed.
- Dendrite is fundamentally suppressed by horizontal centripetal Li plating.
- The thickness fluctuation of the anodes during Li plating/stripping is mitigated.
- Stable cycling performance and high rate performance of Li-metal anodes are achieved.

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Horizontal Centripetal Plating in the Patterned Voids of Li/Graphene Composites for Stable Lithium-Metal Anodes

Aoxuan Wang,1 Xinyue Zhang,1 Ying-Wei Yang,2 Jiaxing Huang,3 Xingjiang Liu,1 and Jiayan Luo1,4,*

SUMMARY
Lithium (Li) metal, the anode of choice for its high energy density, was used before the 1990s but was abandoned because of its dendrite formation. There are many strategies to address the dendrite problems, but the Li growth direction is largely normal to the anodes and there are still chances that the dendrites can cross over the separator. Here, we fundamentally suppress dendrites by designing horizontal centripetal Li plating. In patterned reduced graphene oxide (rGO)/Li anodes, the electric field is detoured to the edges of the patterned anodes. Li nucleates at the void edges of the layered Li separated by rGO sheets and grows horizontal centripetally to fill the voids. The patterned rGO/Li anodes were cycled for more than 2,000 hr and maintained stable voltage profiles at a current density of 10 mA cm⁻². We anticipate that the horizontal centripetally grown behavior could revolutionize the design of high-performance Li-metal batteries.

INTRODUCTION
Lithium (Li)-ion batteries are now the dominant energy to power electronics and are still under development for vehicles and grids.¹ ² Their energy density is proposed to increase to 500 Wh kg⁻¹ by the end this decade. This requires the use of high-energy-density electrodes such as Li, S, and O₂.³ ⁴ ⁵ Li is the anode of choice for its highest theoretical capacity (3,860 mAh g⁻¹) and lowest electrochemical potential (−3.04 V versus standard hydrogen electrode). Li-metal anodes were used in Li rechargeable batteries before the 1990s but were abandoned for safety concerns. Like many other metals, Li tends to form dendrites during deposition. The high reducibility of Li and its uncontrollable deposition result in continued production of a solid electrolyte interface (SEI) layer between Li electrode and electrolyte. The cumulated SEI depletes both Li and electrolyte, limiting the cycling lifetime of the Li batteries. Worse still, there exists a possibility that dendrites can short-circuit the batteries by crossing over the porous separator and reaching the cathodes.⁶ ⁻¹⁹

The Bigger Picture
Li-metal anodes are the ideal anodes for their high energy density, but the safety and cycling stability are obstacles preventing their commercialization. This is due to the high reducibility of Li and its uncontrolled dendritic deposition. In various strategies proposed to solve the dendrite problem, the Li growth direction is largely normal to the anodes, and there are still chances that the dendrites can cross over the separator and short circuit the battery. Moreover, there is large thickness fluctuation of the Li anode during plating and stripping. Herein, we report a fundamentally revolutionary approach to suppressing dendrite by designing horizontal centripetally grown Li-metal anodes with patterned rGO/Li composite anodes. Li nucleates at the edges of the empty area in the patterned anodes and grows horizontal centripetally. The horizontal centripetally grown Li-metal anodes are advantageous with mitigated thickness fluctuation and long cycling stability.
Solid-state electrolytes can prevent Li dendrite from contacting the cathode and ultimately make Li-metal anodes viable. However, the presupposition is that the high solid-solid interface resistance of inorganic solid electrolytes and low ionic conductivity of solid polymer electrolytes have been overcome. Liquid electrolytes with diverse formulas of additives have successfully improved the performance of Li-ion batteries, especially under extreme conditions. The continued quest for effective additives has far to go before depressing the long-lasting Li dendrite growth. Interfacial layers can be inserted between the substrates and electrolytes to stabilize the SEI and prevent dendrites penetrating the separator. However, the mechanical stability and Li\(^+\) diffusivity of the interlayers need to be balanced.

Controlling Li ionic flow and thus the Li growth direction was also attempted. A disordered 3D matrix of polymer nanofiber or glass fiber network was placed on top of current collectors to homogenize the Li ionic flux and guide the Li growth along the fibers. Vertical alignment of channels in anodized aluminum oxide membranes, polyimide layers in nanochannel confinement, and Cu were also designed to confine and isolate ionic flux in the nanochannels. Li plating was also manipulated to face toward the current collectors starting from a conductive layer coated on the separator. Nevertheless, the normal Li growth direction is largely toward the anodes. Herein, we report a fundamentally revolutionary approach to suppress Li dendrite by designing horizontal centripetally grown Li-metal anodes.

**RESULTS AND DISCUSSION**

**Principle of Horizontal Centripetally Grown Li-Metal Anodes**

On conventional current collectors there exist defects such as terraces, kinks, and steps where the electric field is stronger than the rest area and Li nucleation is more concentrated. The uneven Li nucleation results in dendrite growth (Figure 1A). The horizontal centripetally grown Li-metal anodes were realized by patterned reduced graphene oxide (rGO)/Li composite anodes (P-rGO/Li). In the cells with charged P-rGO/Li anodes, the electric field is changed from regular anodes (Figure 1B). In the voids, the electric field is detoured to the edges of the patterned anodes. The Li ionic flow follows the direction of the electric field. Although with a shorter distance, the top surface covered by rGO is less favored for Li deposition and/or dissolution as there is nucleation overpotential for Li to deposit on rGO (Figures S1 and S2). As a result, Li prefers to nucleate at the void edges of the layered Li separated by rGO sheets and grows horizontal centripetally to fill the voids. The horizontal centripetally grown Li-metal anodes are advantageous in several aspects. (1) Anode thickness fluctuation is mitigated as Li deposition takes place in the voids of P-rGO/Li anodes. The available deposition volume can be controlled by tuning the ratio of the open area and thickness of the anodes. (2) The edges of P-rGO/Li are widely exposed and their available rough surface is much larger than the top surface in planar electrodes or patterned Li electrodes, leading to much decreased effective current density and ohmic resistance for Li nucleation and deposition. (3) Unlike the deposition nucleation barrier on Cu or other substrates, Li deposition on itself has no interface energy, ensuring homogeneous Li growth (Figure S2). (4) The Li is laminated by rGO sheets, ensuring high-nucleation sites. Indeed, the horizontal centripetally grown Li-metal anodes show much lower nucleation overpotential than Li (Figure 1C) and non-patterned rGO/Li (Figure S2).

**The Preparation Process of P-rGO/Li Anode**

The P-rGO/Li-metal anodes were prepared by template flash etching of GO films followed by capillary infusion of molten Li between GO sheets (Figures 2 and S3).
GO can be flash etched under excessive flash exposure.\textsuperscript{45–47} With a patterned mask covered on top, the shadow area of GO was left, duplicating the mask. Upon contact with molten Li, the patterned GO films were reduced to rGO and the thickness expanded caused by gas evolved during reduction (Figure S4). Molten Li was absorbed into the inter-sheet space between rGO sheets (Figures S5–S7). The patterns of the composite anodes can be diversified, simply by using different masks (Figure S8). The process can also be adapted to make patterned Na composite anodes (Figure S9) or others with improved performance (Figure S10).

**Surface Morphology Evolution of P-rGO/Li Anode during Charge-Discharge Process**

The horizontal centripetal growth behavior in the patterned Li composite metal anodes can be visualized by monitoring the surface morphology of the anodes after plating different amounts of Li using 1 M LiTFSI in 1,2-dimethoxyethane/1,3-dioxolane (DME/DOL) (1:1) electrolyte with 1% LiNO\(_3\). From the scanning electron microscopy (EM) images, it can be clearly observed that Li was first deposited at the rough patterned edges (Figures 3A and 3B). The open areas in the P-rGO/Li anodes were gradually filled with increased Li plating capacity from 0.5 to 2 mA\(\text{h cm}^{-2}\) (Figures 3C and 3D).
3B–3E). It should be noted that pure Li metal could also be printed with patterns.\textsuperscript{41,43} Li preferred to nucleate at the top of void edges. In our case, the rGO sheets segregated the Li in the bulk composite and roughed the patterned edges, increasing their available Li plating area. Li was deposited not only at the top but also at the middle and bottom of the void edges (Figure S11). The top surface of P-rGO/Li is covered by rGO sheet (Figure S12), which has larger nucleation overpotential than on Li; no Li was found to be deposited on the top of the electrodes. An O-ring separator was used and there was no difference in the electrode morphology between the in/out areas of the O-ring range, which excludes the pressure effect from the separator (Figure S13). Upon increasing the capacity to 3 mAh cm\textsuperscript{-2}, the voids were fully filled with Li. The excess Li was deposited upright at the top of the void areas and formed a convex slope (Figure S14). This again confirms that the top surface of P-rGO/Li is covered by rGO, which is less favorable for Li deposition. During the stripping process, the morphology evolution was reversed and the pores were dilated (Figure S15). Original patterned anodes were recovered after Li was completely stripped (Figures 3F and 3G). After cycling, the surface of the P-rGO/Li electrode maintained smooth formation without protruding Li dendrite (Figure S16). The anode thickness here was 70 \mu m and the open area was 40%. The Li deposited in the void has a loose porous structure (Figure S17). The maximum Li loading amount in the voids of the patterned anodes can be increased by increasing the film thickness (Figures S18 and S19) and open area (Figure S20). The Li content in the P-rGO/Li anodes was 93% (Figure S21), and could be stripped and plated without changing the structure by much (Figure S22).

**Electrochemical Performance**

The P-rGO/Li anodes can serve as both scaffolds for dendrite-free horizontal centripetal Li deposition and Li sources to couple with cathodes. Symmetric cells were first assembled to compare the plating and stripping cycling performance of horizontal centripetally grown anodes with pure Li foils in ether electrolyte with plating and stripping capacity of 1 mAh cm\textsuperscript{-2} (Figure 4A). At current density of 1 mAh cm\textsuperscript{-2}, the cell voltage hysteresis of Li foils was unstable and the cell was shorted after...
400 hr (200 cycles), while in P-rGO/Li cells much smaller voltage hysteresis and stable SEI (Figures S23 and S24; Table S2) were observed and the cells were stable for more than 1,000 hr (500 cycles). The scanning EM images after cycling show that the P-rGO/Li electrode surface was more homogeneous without significant protuberance (Figures S16 and S22), in contrast to mossy dendrites on the Li electrode surface (Figure S25). On increasing the current densities to 2 mA cm$^{-2}$ (Figure S26), 3 mA cm$^{-2}$ (Figure 4B), and 10 mA cm$^{-2}$ (Figure 4C), the P-rGO/Li electrode was able to maintain a more stable plating and stripping voltage profile and lower overpotential than the non-patterned rGO/Li and pure Li anodes. This current density is among the highest values reported for Li-metal anodes (Table S1 and Figure S27). In contrast, the pure Li anode symmetric cells showed much higher overpotential and remarkable fluctuation in the plating and stripping process, failing in the first few tens of cycles at current density of over 3 mA cm$^{-2}$ (Figures 4B and 4C). When decreasing the current density to 0.5 mA cm$^{-2}$, the P-rGO/Li anode symmetric cell can maintain stable, smooth cycling plateaus for as long as 2,000 hr (500 cycles), showing long-term stability (Figure S28). We next performed a voltage profile comparison of Li foil, rGO/Li anode, and P-rGO/Li anode symmetric cell cycling under increasing current density from 0.5 mA cm$^{-2}$ to 5 mA cm$^{-2}$ with fixed capacity of 0.5 mAh cm$^{-2}$ (Figure S29). It can be seen that the P-rGO/Li anodes exhibited flatter plateaus and smaller average voltage hysteresis during the plating and stripping process. The P-rGO electrode also had higher Coulombic efficiency than Cu foil at different current densities (Figure S30). Impedance spectroscopy measurement conducted on the symmetric cells showed that the P-rGO/Li anodes had much smaller resistance than pure Li and rGO/Li anodes (Figure 4D), which is consistent with their lower polarization in plating and stripping voltage profiles. The P-rGO/Li anodes were assembled into a full cell with LiFePO$_4$ cathodes. The cells with the P-rGO/Li anode had higher rate capacity (Figure 4E) and better cycling performance (Figure S31) than the cells with pure and rGO/Li anodes, which is consistent with the
The P-rGO/Li anodes can also match LiFePO₄ cathodes with a high load (\(\text{C}/2\)), showing their practical application for the Li-metal batteries (Figure S32).

In summary, we proposed horizontal centripetally grown Li-metal anodes based on P-rGO/Li composites, which can fundamentally suppress Li dendrites. Li first nucleates at the rough edges of the voids in the patterned anodes and grows horizontal centripetally to fill the empty space. The symmetric cell with P-rGO/Li anodes could match LiFePO₄ cathodes with a high load (\(\text{C}/2\)), showing their practical application for the Li-metal batteries (Figure S32).
be cycled for more than 2,000 hr and was able to maintain a stable plating and stripping voltage profile at a current density of 10 mA cm$^{-2}$. Optimizing the size, shape, and overall area of the patterns and electrode thickness could definitely further improve the electrochemical performance, which is currently under investigation. This strategy paves the way for dendrite-free Li-metal anodes.

**EXPERIMENTAL PROCEDURES**

**Preparation of P-rGO/Li Composite Anodes**

GO solution (2 mg/mL) was prepared by a modified Hummer’s method as reported elsewhere. Densely packed GO films were obtained by vacuum filtration method. Freestanding GO films were then dried at 50°C for 48 hr in a vacuum oven. The flash from the xenon lamp equipped on a common digital camera was used to reduce the GO film in the air circumstance. The mask covered on the top of the GO film was obtained from MTI. To remove the exposed part, we used multiple flashes until the GO net was obtained. The patterned GO films were then transferred to an argon-filled glovebox with O$_2$ level <0.2 ppm. Bulk Li (99.7%, Aladdin) metal was heated to ~400°C in a Ni boat in a muffle furnace placed in the glovebox. Patterned GO films were brought into contact with molten Li, which instantaneously underwent thermally triggered self-propagating reduction to form a porous patterned rGO structure. Meanwhile Li was absorbed into the patterned rGO films to yield a patterned rGO/Li (P-rGO/Li) composite anode.

**Characterization**

Scanning EM (Hitachi S4800, Japan) and transmission EM (JEOL, 2100F) were employed for microscope characterization. Before conducting scanning EM studies of the cycled electrodes, the batteries were first disassembled in the glovebox and gently rinsed in DOL to remove residual Li salts. Raman spectra were recorded using a WITEC Raman spectrometer with a 531-nm excitation laser. X-ray diffraction patterns were recorded on a Rigaku D/max-2500B2+/PCX system with Cu-K$_\alpha$ radiation, and the electrode was loaded onto a glass slide and covered with Kapton tape during measurements to avoid direct contact with air. X-ray photoelectron spectroscopy spectra were collected on an SSI SProbe XPS spectrometer with an Al (K$_\alpha$) source.

**Electrochemistry**

To study the Li stripping/plating processes, we loaded the electrodes into 2032-type coin cells in both symmetric and full cell configurations. The anodes used in this experiment were Li foil, rGO/Li, or P-rGO/Li. The cathode was prepared by mixing LiFePO$_4$ (LFP; MTI), Super P (MTI), and polyvinylidene fluoride (MTI) at the ratio of 7:2:1 with N-methyl-2-pyrrolidone as the solvent. The electrolyte used for the symmetric cells was 1 M lithium bis(trifluoromethanesulfonyl)limide (99.95%, Sigma-Aldrich) in a mixture of 1,3-dioxolane (Sigma-Aldrich) and 1,2-dimethoxymethane (1:1 by volume, Sigma-Aldrich) with 1 wt % LiNO$_3$. LiPF$_6$ (1 M) in EC/DEC (ethylene carbonate/diethyl carbonate, 1:1 by volume) was used as the electrolyte for the full cells. Celgard 2325 was used as the separator. Galvanostatic cycling was conducted on a LAND-CT2001A 8-channel battery tester. The electrochemical impedance spectroscopy measurements were carried out on a Solartron 1400 cell test system.

**SUPPLEMENTAL INFORMATION**

Supplemental Information includes 32 figures and 2 tables and can be found with this article online at https://doi.org/10.1016/j.chempr.2018.06.017.
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AUTHOR CONTRIBUTIONS

A.W. carried out most of the experimental work. X.Z. assisted with sample characterization. J.L. proposed and supervised the project and wrote the manuscript. A.W., X.Z., Y.-W.Y., J.H., X.L., and J.L. discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES AND NOTES


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