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Lithium-Metal Anodes Working at 60 mA cm⁻² and 60 mAh cm⁻² through Nanoscale Lithium-Ion Adsorbing

Lei Ye⁺, Meng Liao⁺, Xiangran Cheng, Xufeng Zhou, Yang Zhao, Yibei Yang, Chengqiang Tang, Hao Sun, Yue Gao, Bingjie Wang,* and Huisheng Peng*

Abstract: Achieving high-current-density and high-areacapacity operation of Li metal anodes offers promising opportunities for high-performing next-generation batteries. However, high-rate Li deposition suffers from undesired Liion depletion especially at the electrolyte-anode interface, which compromises achievable capacity and lifetime. Here, electronegative graphene quantum dots are synthesized and assembled into an ultra-thin overlayer capable of efficient Liion depletion. The protected Li anode achieves long-term reversible Li plating/stripping over 1000 h at both superior current density of 60 mA cm⁻² and areal capacity of 60 mAh cm⁻². Implementation of the protected anode allows for the construction of Li-air full battery with both enhanced rate capability and cycling performance.

he increasing ubiquity of electric vehicles and smart grids has motivated intensive researches on high-energy-density batteries beyond Li-ion ones.^[1-4] Li-metal anodes have a high specific capacity and a low potential, thus enabling high cell energy densities when coupled with high-capacity cathodes such as oxygen, sulfur, and metal fluorides.^[5-7] To realize high power outputs and fast charging of these advanced battery systems, superior current densities over 30 mA cm⁻² (e.g., over 3 C rate, full charge within 20 minutes for a 500 $Wh kg^{-1}$ cell, the goal of the United States Department of Energy) are required.^[8,9] However, due to the accelerated electrochemical reduction of Li-ions (Li⁺) at such high current densities, Li⁺ depletion on the anode surface and Li⁺ agglomeration around hotspots are inevitable with nonuniform Li deposition, making dendrites and dead Li easy to grow (Figures 1 a and S1).^[10,11] These undesirable factors in turn cause an unstable Coulombic efficiency (CE) and exacerbate the capacity fading of Li-metal-based full batteries under practical conditions.[12,13]

Homogenizing the Li⁺ concentration represents an increasingly popular solution to the above problems consid-

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 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202106047.

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ering the diffusion-coupled reaction nature of Li deposition. To date, efficacious strategies including separator modification,^[14,15] electrode layout design,^[16–18] and high concentration electrolyte^[19,20] have been proposed to regulate the macroscopic Li⁺ concentration within the whole electrolyte-filled areas. However, compared with the bulk electrolyte, the electrolyte-anode interface is less involved while more vulnerable to the inhomogeneous Li⁺ concentration due to the Li⁺ depletion effect especially at high current densities.^[10,11] Consequently, the existing Li anodes with high capacities ($\geq 10 \text{ mAh cm}^{-2}$) can only be cycled ($\geq 1000 \text{ h}$) at limited current densities ($\leq 10 \text{ mA cm}^{-2}$).^[21] Hence, it is significant while challenging to efficiently regulate Li⁺ concentration at the electrolyte-anode interface for practical Limetal anodes.

Here, we first present an ultrathin Li⁺ adsorbing layer (LAL) comprising graphene quantum dots with surface polar functional groups on the Li-metal surface to tackle the above limitations (Figures 1 b,c). The strong Li⁺ affinity from electronegative quantum dots in the LALs renders accurate spatial confinement of Li⁺ flux within the electrolyte-anode interface and increases the local Li⁺ concentration at the nanoscale, thus relieving the Li⁺ depletion at high current densities. Meanwhile, Li⁺ can penetrate through the LAL, leading to the continuous Li⁺ adsorbing effect and dendritefree Li deposition (Figure S1). As a result, a long-term reversible Li plating/stripping over 1000 h has been achieved at both high current density (60 mA cm^{-2}) and areal capacity (60 mAh cm^{-2}) , far exceeding the available Li anodes. Implementation of the LAL-incorporated Li anode allows for the construction of Li-air batteries with both enhanced rate capability and cycling performance than that with a bare Li anode.

As the nanoscale building blocks for the LAL, graphene quantum dots, comprising nanocrystalline carbon cores and surface polar functional groups, were prepared via a one-step, bottom-up synthesis strategy (Figures 1 c and S2).^[22] Graphene fragments in the core exhibited typical sizes of 3-5 nm (Figure 1d), average thickness of $\approx 2 \text{ nm}$ (Figure S3), and normal size distribution (Figure 1e). The peak centered at 1573 cm⁻¹ in Raman spectrum (Figure S4) was assigned to graphitic carbons with localized sp² electrons that could induce attraction forces toward Li⁺ (Figure 1c, right panel). The fringe-rich feature of carbogenic cores also enabled better surface grafting for enhanced Li⁺ affinity, as indicated by a total electronegative element (O, N, and S) content of 21.1 atom% (Figures S5 and S6). Electronegative functional groups containing -OH, -NH₂, C=O/C=N, C=C, and C=S bonds were further determined by Fourier transform infrared

^[*] L. Ye,^[+] M. Liao,^[+] X. Cheng, X. Zhou, Dr. Y. Zhao, Y. Yang, C. Tang, Dr. H. Sun, Dr. Y. Gao, Dr. B. Wang, Prof. H. Peng State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University Shanghai 200438 (China) E-mail: wangbingjie@fudan.edu.cn penghs@fudan.edu.cn
[⁺] These authors contributed equally to this work.



Figure 1. (a) and (b) Schematics of the Li⁺ depletion in bare Li anode and the Li⁺ adsorbing in LAL/Li anode upon Li deposition, respectively. (c) Schematic showing the preparation process (left panels) and the design rationale (right panel) of the graphene quantum dot building blocks for the LAL. (d) Transmission electron microscopy (TEM) image of the synthesized graphene quantum dots (inset, high-resolution TEM image showing lattice fringe). (e) Size distribution of the graphene quantum dots. (f) FTIR spectra of the LAL.

spectroscopy (FTIR, Figure 1 f).^[22] Benefiting from their abundant polar groups, the as-synthesized quantum dots could form uniform dispersions in common solvents with good film-forming ability on Li substrates.

The LAL overlayer on Li anodes was prepared by spincasting a sulfoxide/acetonitrile solution of the as-prepared graphene quantum dots ($\approx 0.6 \text{ mg mL}^{-1}$). The thickness of the spin-casted LAL was optimized (details in Note S2 and Figure S7) and the resulting surface of the LAL/Li anode was uniform and smooth (Figures S8-S11). A typical thickness of ≈ 60 nm was measured by both atomic force microscopy (Figure S12) and step profiler (Figure S7). Compared with most artificial protective layers with the thickness on the order of micrometers, the ultrathin LAL could protect Li anodes with the minimized sacrifice of both actual volumetric and gravimetric energy densities.^[3] Despite of the ultrathin thickness, the LAL containing graphene domains showed a high modulus of 6.22 GPa, which was deemed sufficient for Li dendrite blocking (Figure S13).^[23] In addition, chemical adhesion (O-Li and NH-Li), as evidenced by X-ray photoelectron spectroscopy (XPS) depth profiling and FTIR results, could be formed between the coated LAL and Limetal for the enhanced interfacial contact against exfoliation during Li plating/stripping in the resulting LAL/Li anodes (Figures S14 and S15). Nyquist plots of the LAL/Li electrodes displayed only a slight change after a four-month rest, further indicating the chemical stability (Figure S16).

Inherited from the graphene quantum dots with strong Li^+ affinity, the LAL exhibited enhanced interaction with Li at

the molecular level (i.e., graphene of -4.62 eV, -OH of -4.79 eV, -COOH of -5.54 eV, C=O of -4.98 eV, and O-, N-, S-containing group of -5.49 eV), compared with -1.89 eV between Li and routine Cu substrate (Figures 2 a,b, and S17). This strong interaction facilitated the adsorption of Li⁺ flux and the initial Li deposition in a uniform manner by reducing the nucleation overpotential (Figure S18). Further, the surface polar groups together with sp² graphene domain cores in the synthesized quantum dots increased localized negative charges, as indicated by the 2D charge density profiles, paving the way for nanoscale Li⁺ flux confinement at the electrolyteanode interface (Figure S19). The nanoscale Li⁺ adsorbing in the LAL was then verified in a visualized clue by finite element simulation (Figure 2c). Even under a high-rate (20 mA cm⁻²) Li plating, apparent Li⁺ enrichment and compressed concentration polarization could still be observed above the vicinity of the LAL/Li anode. The cross-sectional profile along the normal X direction indicated a homogeneously distributed Li⁺ concentration across the LAL/Li surface (Figure 2e). In stark contrast, lower Li⁺ concentration, especially at the dendrite tips, was observed along with nonuniform Li⁺ flux across the bare Li surface (Figures 2 d,e). The growth of Li dendrites would preferentially occur in this region of Li⁺ depletion due to the intense concentration polarization.^[10,11]

The Li⁺ adsorption measurement experimentally manifested that the LAL could induce a higher ionic concentration over bulk solution (Table S1). The zeta potential of the dispersed LAL in DOL/DME (1:1 vt%) shifted from -24.5 to



Figure 2. (a) Atomic model of the synthesized graphene quantum dots in the LAL. (b) Binding energies of Li atoms with the LAL by density functional theory (DFT) calculations. G represents graphene. (c) and (d) Li⁺ distribution of the LAL/Li and bare Li by COMSOL simulation, respectively. (e) Li⁺ concentration profiles at the LAL/Li and bare Li surfaces along X direction extracted from (c) and (d). (f) LSV profiles of LAL/Li and bare Li electrodes.

-5.8 mV when 1 M LiTFSI was added, further validating the Li⁺ adsorbing effect. Moreover, the LAL/Li anode exhibited a Li⁺ transference number (t_{Li+}) of 0.57 with 1 M LiTFSI in DOL/DME (1:1 vt%) as the electrolyte, which was higher than 0.27 for bare Li and appropriately 0.3–0.4 for previously reported modified Li anodes (Figure S20).^[4,14] Similar to the measurement results at static state, linear sweep voltammetry (LSV) of LAL/Li also showed an apparently increased current density over bare Li electrode, indicating a higher local Li⁺ concentration within LAL/Li (Figure 2 f). Moreover, the Li⁺ adsorbing effect of LAL/Li proved to be sustainable at a high diffusion-limited current (Figure S21).

To examine the morphology of the LAL/Li and bare Li anodes, symmetric cells that worked at varied current densities and capacities, were disassembled after cycling and traced by scanning electron microscope (SEM). The cycled bare Li anodes demonstrated rough surfaces with irregular branched Li, which was aggravated upon the increase of applied current densities (from 1 to 40 mAcm⁻²) and areal capacity (from 1 to 20 mAhcm⁻², Figures S22 and S23). By contrast, smooth surfaces and densely packed Li were

observed in all cvcled LAL/Li anodes (Figures S22 and S24). Impressively, this smooth morphology was sustained even after 50 cycles of Li plating/stripping at a deep-level capacity of 60 mAh cm⁻² at 60 mA cm^{-2} (Figure 3a). The LAL was kept on the surface of the LAL/Li anode, as indicated by its cross-sectional SEM image (Figure S25). Contrastingly, dendritic Li shot out from bare Li anodes when tested under the same conditions (Figure 3b). Further, with increasing Li deposition from 10 to 60 mAh cm^{-2} , the LAL/Li samples constantly kept reduced thick-48.8 nesses (from to $301.8 \,\mu\text{m}$) than those of Cu/Li (from 61.2 to 353.1 µm, Figures S26 and S27). This evolution of thickness indicated that Li deposition in the LAL/Li followed а favorable bottom-up pattern durable of high capacity with reduced porous and dendritic structures inside.[3,14]

Consistent with the Li deposition morphology, a homogeneous SEI was identified by Raman map-

ping on the LAL/Li anodes after the removal of electrolyte (Figure 3c). Contrastingly, the surface of bare Li was rather heterogeneous (Figures 3d and S28) with a larger percentage of ROLi (13.9%), which was deemed insufficient for Li⁺ diffusion and vulnerable to drastic volume change (Figures 3 f and S29). $\ensuremath{^{[24]}}$ The electronegative group such as -NH- in the LAL/Li could be verified by N 1s spectra after cycling (Figure 3e). This suggested that the LAL had participated the formation of the initial SEI and kept intact in the resulting SEI upon cycling. Notably, as shown in F 1s and Li 1s XPS spectra, the LAL was found to induce a LiF-rich SEI in the LAL/Li electrodes. The difference in SEI composition originated from the LAL with hydrogen-bond donors (-NH₂/-NH- groups) adjacent to a hydrogen-bond acceptor (TFSI-) in the electrolyte, which resulted in accelerated decomposition of TFSI- into LiF.^[25,26] The LiF with low inplane diffusion barrier is beneficial for fast lateral Li⁺ diffusion and large surface energy, and therefore contributes to improved Li⁺ flux and kinetics in the SEI of LAL/Li anodes for smooth Li deposition at high rate.^[24,25]



Figure 3. (a) and (b) SEM images of the LAL/Li and bare Li anodes after 50 cycles at 60 mAcm⁻² and 60 mAhcm⁻², respectively. (c) and (d) Raman mappings of the signals ranged from 200 to 300 cm⁻¹ of the Li SEI that was formed on the LAL/Li and bare Li anodes after cycling, respectively. (e) and (f) XPS spectra of the Li SEI that was formed on the LAL/Li and bare Li anodes after cycling, respectively. The binding energy values were all calibrated using the adventitious C 1s peak at 284.6 eV.

To evaluate the interface stability of electrodes, symmetric batteries based on the LAL/Li or bare Li electrodes were cycled at varied current densities from 1 to 40 mA cm⁻² and areal capacities from 1 to 20 mAh cm⁻² (Figures 4a and S30). As a result, the LAL/Li electrodes exhibited reduced plating/ stripping overpotentials and enhanced cycling life (up to 2800 h) than bare Li electrodes in all the test conditions. Impressively, even at ultrahigh current density (60 mA cm⁻²) and areal capacity (60 mAh cm⁻²), batteries using the LAL/Li anodes exhibited long-term stability for over 1000 h (Figure 4b). Magnified voltage profiles of the LAL/Li anodes showed a regular and flat shape throughout the cycling process without any potential short-circuit condition. In contrast, anomalous fluctuations in voltage with large overpotential over 1 V appeared in bare Li anodes after only 50hour cycles. Noting that the performance of LAL/Li anode outperformed that of Li anodes stabilized by other strategies (Figure 4c and Table S2). Using graphene quantum dots for the fabrication of LALs has several advantages: 1) Their small dimensions with large number of edge sites could afford enhanced surface grafting than 3D or 2D nanomaterials to afford superior Li⁺ affinity.^[22] 2) Their high solubility and easy handling were beneficial for the achievement of ultra-thin LALs. 3) The chemical composition of resulting LALs could be well controlled by a bottom-up synthesis using designed molecular precursors.

The practical realization of the rate was further elucidated in Figure 4d. Upon continuous cycling with increasing current densities from 1 to 60 mA cm⁻², the overpotential of the LAL/ Li electrodes was increased only marginally at high rates and



Figure 4. (a) Galvanostatic cycling profiles of symmetric cells with the LAL/Li electrode or bare Li electrode at 20 mAh cm⁻² and 40 mA cm⁻². (b) Galvanostatic cycling profiles of symmetric cells with the LAL/Li electrode or bare Li electrode at 60 mAh cm⁻² and 60 mA cm⁻². (c) Comparison of the current density, areal capacity, and cycle life of symmetric cells with the LAL/Li electrode and those of previously reported excellent Li-metal anodes stabilized by various strategies.^[27-32] (d) Li plating/stripping overpotentials of the LAL/Li and bare Li electrodes at a spectrum of current densities from 1 to 60 mA cm⁻². (e) Nyquist plots of the symmetric batteries of LAL/Li and bare Li electrodes after the initial cycle and 50 cycles at 60 mA cm⁻² and 60 mAh cm⁻², respectively. (f) CE of Li plating/stripping on the LAL/Cu and bare Cu electrodes at 1 mA cm⁻².

immediately recovered with their reversal. In contrast, the bare Li electrodes displayed an undesirable, larger overpotential at each rate. The LAL/Li electrode also presented lower and more stable interfacial resistance than that of a bare Li electrode (Figure 4e and Table S3). Coulombic efficiencies (CEs) were further recorded from Li || Cu batteries with and without incorporation of the LAL. A higher initial CE of 92.7% from the LAL-incorporated sample at 1 mAh cm⁻² and 1 mA cm⁻², compared with 65.3% from the bare Li || Cu battery, indicated a reduced electrolyte consumption (Figure 4f). The LAL-incorporated samples delivered much higher CEs than the Li || Cu batteries during cycling upon a spectrum of current densities and areal capacities (Figures S31 and S32). Further, the LAL also

demonstrated effectiveness in the commercial carbonatebased electrolytes (i.e., 1 M LiPF₆ in EC/DEC, Figure S33).

As a proof of concept, Li-air batteries were assembled using the LAL/Li or bare Li anodes, carbon nanotube aircathodes, and ether-based electrolyte (1 M LiTF in TEGDME with LiI redox mediator, details in Note S5). A cut-off capacity of 500 mAhg⁻¹ was employed at 1000 mAg⁻¹ (based on the mass of cathode material). The discharge product in cathode was proved to be Li_2O_2 by X-ray diffraction analysis (Figure S34) and presented high reversibility as revealed by its decomposition upon recharge (Figure S35). The LAL/Li-air battery could be stably cycled for over 450 cycles in ambient air with highly overlapped voltage profiles and steady discharge plateaus at ≈ 2.8 V (Figure-



Figure 5. (a) and (b) Discharge/charge voltage profiles (1000 mA g⁻¹ and 500 mAh g⁻¹) of Li-air batteries with the LAL/Li and bare Li anodes, respectively. (c) Corresponding discharge plateaus and specific capacities of the Li-air batteries in (a) and (b). (d) Rate performances of the Li-air batteries.

s 5 a,c). In contrast, the bare Li-air battery collapsed within 100 cycles with a sharply decreased discharge plateau to less than 2.2 V (Figures 5 b,c). Meanwhile, the LAL/Li-air battery exhibited enhanced rate performance, i.e., a slight change in discharge plateau from 2.85 to 2.62 V with current densities from 100 to 2000 mA g^{-1} (Figure 5 d). The above wellperforming Li-air batteries with the LAL/Li anodes rooted from the LAL mediated, dense Li deposition rather than mossy dendrites in bare Li anodes (Figure S36). This dense structure effectively decreased the exposure and corrosion of Li-metal toward oxygen or moisture in ambient air. Correspondingly, reduced side reaction products in air (e.g., LiOH and Li₂CO₃) on the LAL/Li anode surface (Figures S37 and S38) were observed with a limited increase in the internal resistance of the LAL/Li-air battery after cycling (Figure S39).

In conclusion, a facile and scalable strategy for stable Limetal anodes at ultrahigh current density and areal capacity is demonstrated by preparing a Li⁺ adsorbing layer comprising nanoscale building blocks of electronegative graphene quantum dots. The ultrathin Li⁺ adsorbing layer can relieve the Li anode surface from Li⁺ depletion on one hand and does not add weight and bulk to the composite anode on the other. The obtained LAL/Li anode could stably cycle for over 1000 h at superior conditions of 60 mA cm⁻² and 60 mAh cm⁻², far exceeding available Li anodes. This interface design may push the boundary of high-performing Li anodes to fully unlock the potential of next-generation, Li-metal-based batteries.

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Conflict of Interest

The authors declare no conflict of interest.

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