Supporting Information for

Revealing Principles for Design of Lean-Electrolyte Lithium Metal Anode via In Situ Spectroscopy

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Fig. S1 (a) Charge-discharge curves before Li plating/stripping. This pre-activation process helped to stabilize the SEI layer. The current density was set as 0.2 mA cm⁻² from 0.01 V to 1V. (b) Charge-discharge curves and (c) cyclic stability of L-DG at the cut-off voltages of 0.5 V and 1.0 V. For the Li stripping process, data show a negligible areal capacity of 0.018 mAh cm⁻² in the range of 0.5 V-1.0 V (blue line in Fig. S2b). The stable cycling at different cut-off voltages also confirms that a cut-off voltage of 0.5 V is suitable for the Li plating/stripping tests.



Fig. S2 SEM image of 3D high-surface-area graphene (H-DG).



Fig. S3 Charge-discharge curves of Li plating/stripping with flooded electrolyte within a 3D graphene host. The current density is 1 mA cm⁻² and the areal capacity is 1 mAh cm⁻².



Fig. S4 (a) TEM image of 3D graphene (G) heated at 2800 °C and (b) its simulated ordered graphene structure. Few defects can be observed from the images.



Fig. S5 (a) N_2 adsorption-desorption isotherms (77 K) measured for H-DG and L-DG; (b) Pore size distributions dV(D)/dD (where V is the volume of liquid adsorbate and D is the pore size) obtained for L-DG and H-DG. H-DG contains an abundant amount of micropores around ~1.4 nm and mesopores around ~3-7 nm. In contrast, these pores disappear in L-DG due to the high-temperature treatment that re-arranges the graphene units.



Fig. S6 Raman spectra of L-G heated at 2800 °C.



Fig. S7 Comparison of nucleation overpotentials for G-1500, G-2000 and G-2800. (a) Raman spectra of G-1500, G-2000 and G-2800; (b) Discharge curves at 50 μ A cm⁻²; (c) The nucleation overpotentials obtained for G-1500, G-2000 and G-2800. High-temperature treatment is an effective way to control the defect density in carbon materials. The defect density decreases with increasing heating temperature, as indentified by the I_D/I_G ratio in Fig. S7a. As expected, G-1500 shows the lowest nucleation overpotential of 15.7 mV. In contrast, G-2800 exhibits a much higher overpotential of 19.9 mV. These results confirm that Li tends to nucleate on the defective sites.



Fig. S8 Calculation of the exchange current densities in the linear region and Tafel region. (a) Discharge curves obtained for L-DG from 50 μ A cm⁻² to 90 μ A cm⁻²; (b) Calculation of the nucleation overpotential; (c) Discharge curves obtained for L-DG from 200 μ A cm⁻² to 1000 μ A cm⁻²; (d) The relationship between the current density and overpotential; A linear relationship is observed in the range from 50 μ A cm⁻² to 90 μ A cm⁻² (as shown in the inset formula); (e) linear scan voltammetry (LSV) plots for L-DG and G at 10 mV s⁻¹; (f) The Tafel plots for L-DG and G.



Fig. S9 The binding and repulsion energy of carbon vacancy for Li atom. (a) Li on pristine graphene, repulsion energy is 0.34 eV; (b-d) The binding energies of C2, C3, C4 vacancy for Li.



Fig. S10 Scheme illustrating Li nucleation and deposition on the defective carbon (L-DG) and non-defective carbon (L-G) hosts. Li tends to nucleate over the whole defective surface of L-DG, and the uniform Li seeds guide the formation of uniform and smooth Li deposits. In contrast, the nucleation sites for Li plating are isolated and randomly distributed on the non-defective graphene units, which leads to uneven Li deposition.



Fig. S11 Typical charge-discharge curves obtained for (a) L-DG and (b) H-DG from 20th to 40th cycles. Each charge-discharge cycle was used to calculate the coulombic efficiency (CE%) in Figure 4a.



Fig. S12 Typical fitting of the EIS plots for L-DG at the (a) 1st cycle and (b) 22th cycle. R_{Ω} is the ohmic/internal resistance, Ω cm²; R_{ct} is defined as the interfacial resistance, Ω cm²; CPE is defined as a constant phase element, a parameter that describes the capacitance; W_s is the Warburg resistance, Ω cm² s^{-1/2}, which is related to the ionic diffusion.



Fig. S13 The cycled cells of L-DG and H-DG for NMR test. (a) The cycling stability of Li plating/stripping on H-DG and L-DG at 1 mA cm⁻²; (b) Charge-discharge curves of L-DG and H-DG at the 40th cycle.



Fig. S14 Charge-discharge curves for L-DG and H-DG at the initial cycles. The current density is 1 mA cm⁻² with an areal capacity of 1 mAh cm⁻².



Fig. S15 Voltage hysteresis of L-DG/Li and H-DG/Li symmetric cells.



Fig. S16 Charge-discharge curves of (a) L-DG/Li//S and (b) H-DG/Li//S cells at different cycles with flooded electrolyte. The electrolyte volume is 100μ L.



Figure S17 Charge-discharge curves of L-DG/Li//S and H-DG/Li//S cells under lean electrolyte conditions. L-DG/Li//S battery at (a) different rates and (b) different cycles; H-DG/Li//S battery at (c) different rates and (d) different cycles; The electrolyte volume is 10 μ L.