Supplementary Information for

Graphite prelithiation by solid electrochemical corrosion of lithium metal with superficial mosaic structure

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Author contributions

Experiments were conceived by S.-Y. Y, X.-Y. Y and Z.-W. F.; electrochemical performance assessments, mechanism characterizations and manuscript writing were done by S.-Y. Y; D.-L. W, H.-Y. X and Y.Q. helped with the sample preparation; Z.-W.F. commented on the manuscript.

Acknowledgement

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Experimental Section

Sample preparation. The layer of LiPON was prepared by radio frequency (RF) magnetron sputtering of a Li_3PO_4 target in the plasma of nitrogen. Lithium metal was evaporated by a thermal deposition system, in which the thickness of film can be monitored by a quartz crystal microbalance inside. Preparation and transfer of samples are all employed in the dry room with a dew point lower than -50 °C. Gr-LiPON was prepared by just depositing an ultrathin layer of LiPON (30 nm) on the bare graphite anode (about 2.0 mAh cm^{-2}), whose cycle performance and EIS analysis have been done to compare with counterparts of Gr. Sample of pGr-S was prepared by evaporating

a 1.25 μm-thickness of lithium film on Gr-LiPON electrode and being shelving in argon-filled glove box for 24 hours before electrochemical tests and characterizations. And pGr-L was prepared by depositing the lithium film (1.25 μm) on the pristine graphite anode and being immersed into liquid electrolyte (1M $LiPF_6$ EC/DMC) for 24 hours. Then the sample was rinsed by solvent of dimethyl carbonate (DMC), dried and used for electrochemical tests and characterizations.

Materials characterization. Samples have been studied by high-solution optical microscope (Gaopin, GP-660V), scanning electron microscopy (Hitachi, Regulus 8100), X-ray diffraction (D8 Advance), Raman microscopy (Renishaw, invia reflex), Auger electron spectroscopy (PHI 710), Time-of-flight secondary ion mass spectrometry (PHI nano TOF II) and X-ray Photoelectron Spectroscopy (PHI 5000 Versaprobe III). Depth profile of XPS was performed by the source of argon ion with the etching depth of 25 nm each time, while the total etching depth for TOF-SIMS is 50 nm, all calibrated by the standard film of SiO_2.

Electrochemical measurements. A water-based slurry of graphite (95 wt%), super P (1.5 wt%), carboxy methyl cellulose (1.5 wt%) and styrene-butadiene rubber binder (2 wt%) was coated on the copper foil as anode with a single-layer loading of 6.0 mg cm^{-2}. While a slurry of active material ($LiCoO_2$), acetylene black (AB) carbon and polyvinylidene difluoride mixed by 96.8:2:1.2 in the solvent of N-methyl-2-pyrrolidone was spread on the aluminum foil as cathodes with the active mass loadings of 12.1 mg cm^{-2} for the single layer of LCO. $LiPF_6$ in ethylene carbonate (EC)/ dimethyl carbonate

(DMC) (1.0 M; v/v = 1:1) was employed as the liquid electrolyte for all cells in this study. Coin cells of CR2032-type were assembled in the glove box filled by argon. Electrochemical measurements were all performed on the battery tester of Neware.

Simulation method. 2D models for two kinds of anode surface have been constructed in nanoscale, physical fields of solid mechanics and heat conduction in solids have been chosen to study. COMSOL Multiphysics 5.4 was used for all the simulations.

Figures

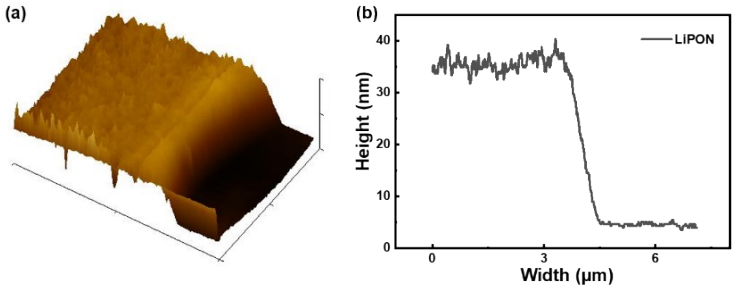

Fig. S1 AFM images of silicon wafer sputtered with the film of LiPON.

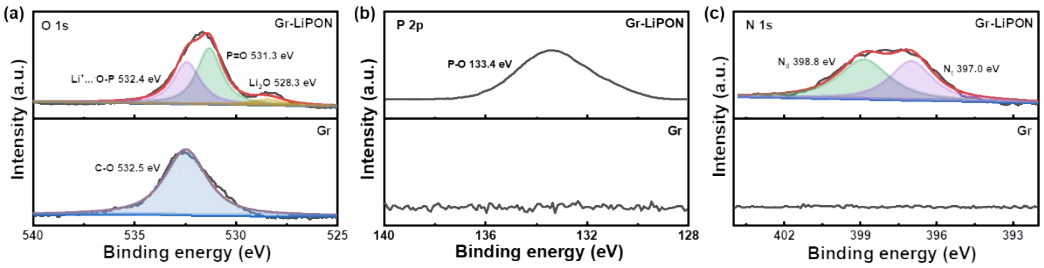

Fig. S2 XPS O 1s, P 2p, and N 1s spectra for pristine graphite (Gr) and graphite with LiPON coating (Gr-LiPON).

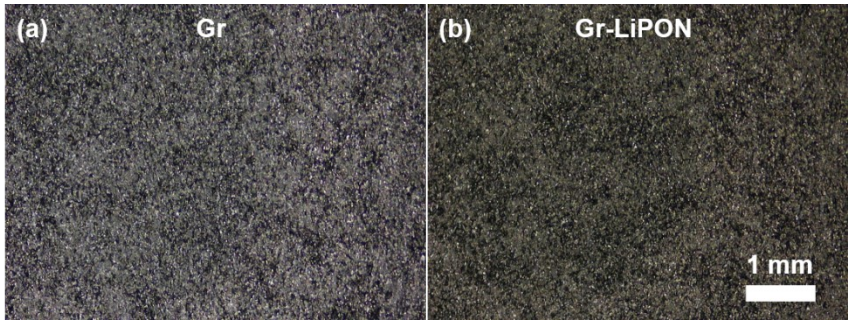

Fig. S3 High-solution optical microscope images of (a) pristine and (b) LiPON-coated graphite.

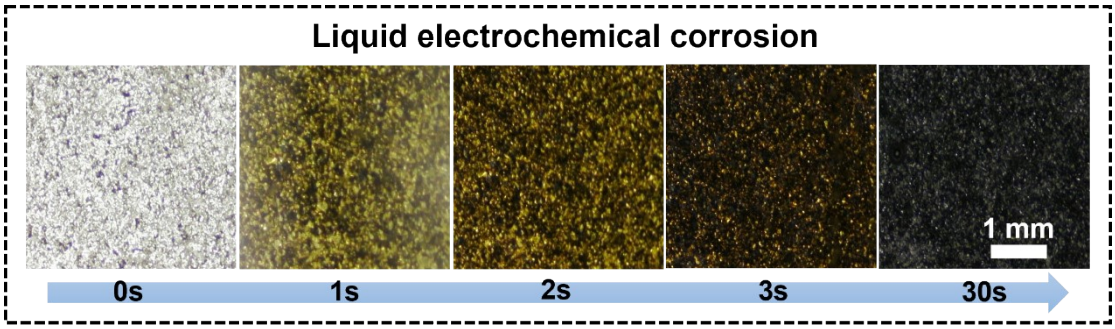

Fig. S4 Prelithiation process of liquid electrochemical corrosion for graphite under high-solution optical microscope.

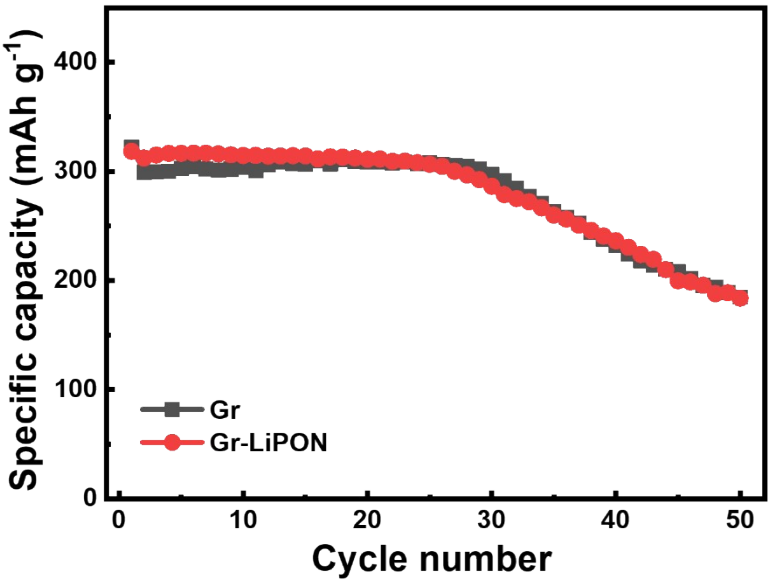

Fig. S5 The cycle performances of pristine and LiPON-coated graphite.

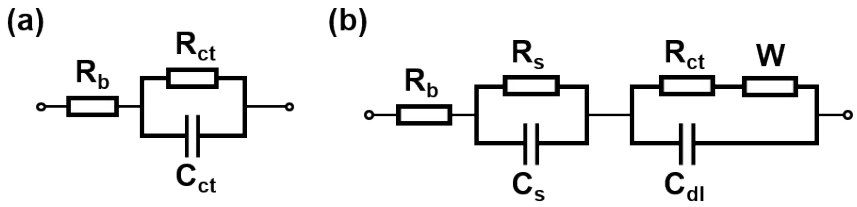

Fig. S6 The equivalent circuits of EIS analysis for (a) pristine graphite at open circuit and (b) other anodes.

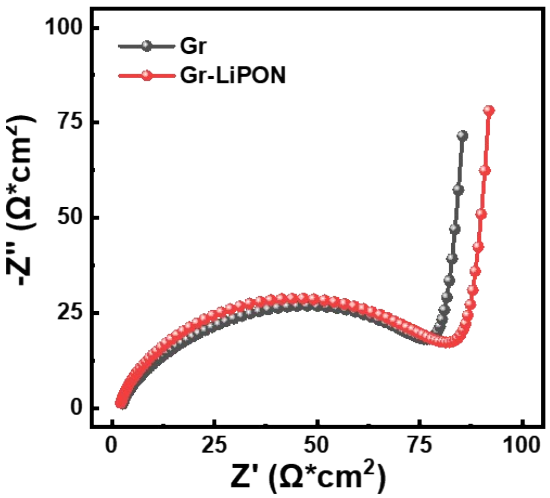

Fig. S7 The EIS results of pristine and LiPON-coated graphite before cycle.

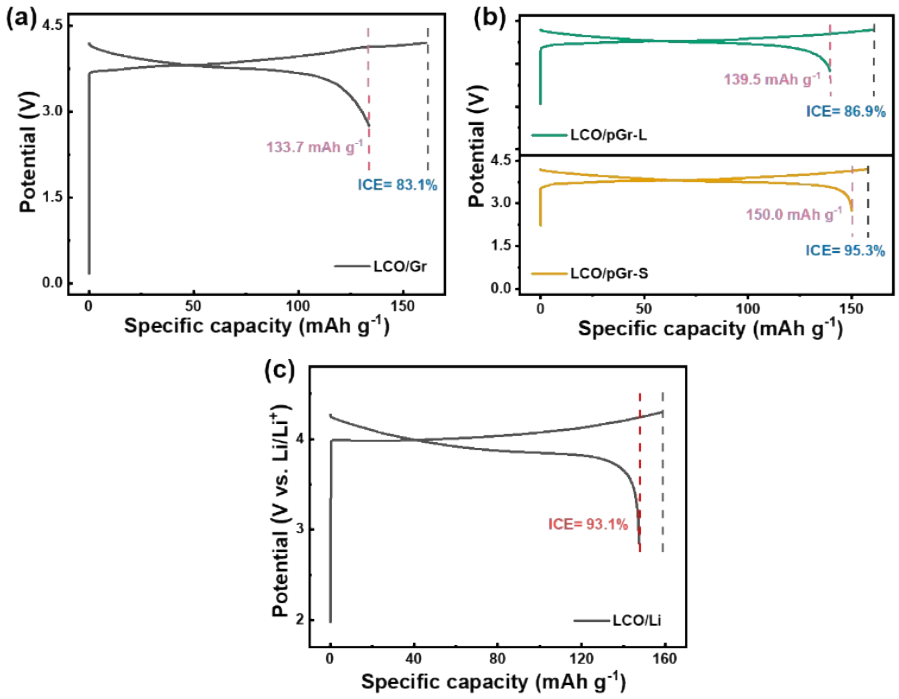

Fig. S8 Charge-discharge curves for full-cells of (a) pristine and (b) prelithiated anodes when paired with LCO cathodes as well as (c) the half-cell of LCO.

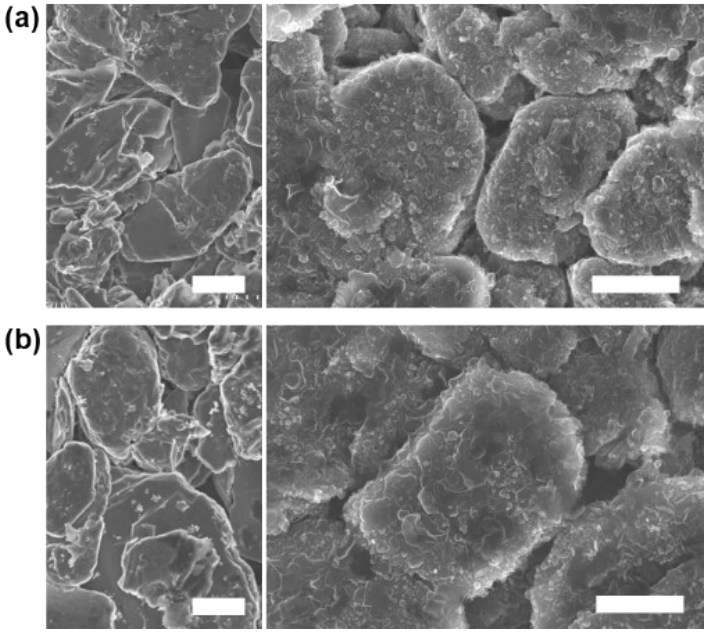

Fig. S9 SEM images of (a) pristine and (b) LiPON-coated graphite before (left) and after (right) lithium deposition (scale bars all point to 5 μm).

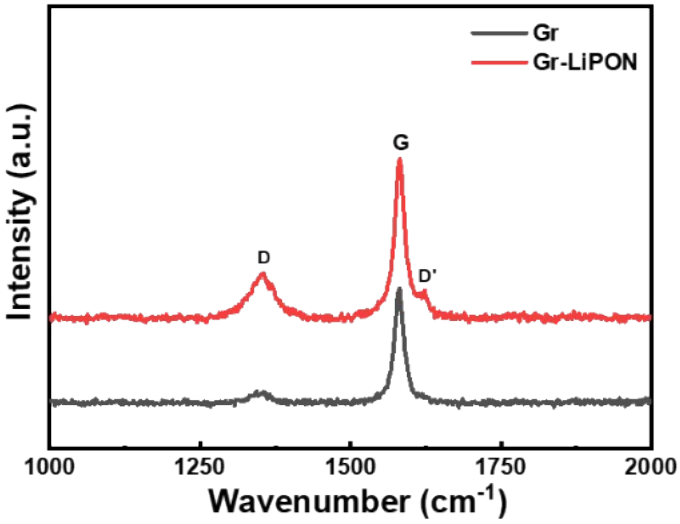

Fig. S10 Raman spectra of pristine and LiPON-coated graphite.

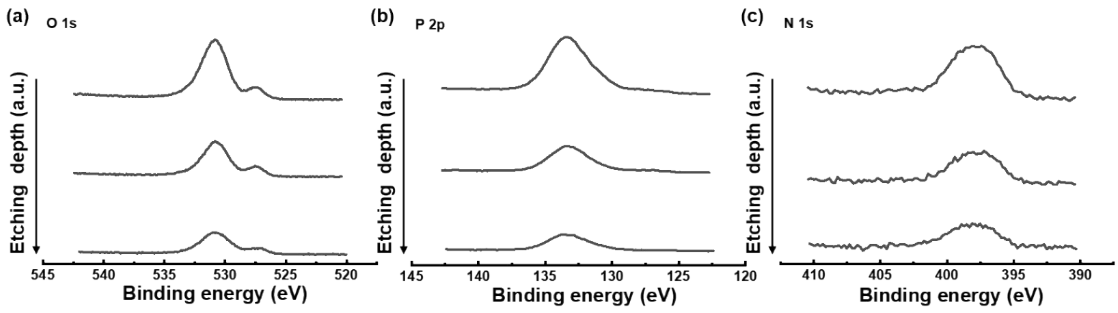

Fig. S11 XPS depth profiling results (etching two times in total) of O 1s, P 2p and N 1s for the LiPON-coated graphite.

Tables

Table S1. The impedance values of pristine and prelithiated anodes.

Unit		Pristin	LEC	SEC
Before cycle	**Rb**	1.552	2.456	1.722
	Rs	/	17.03	16.92
	Rct	87.69	17.02	2.666
After cycle	**Rb**	2.216	2.858	2.223
	Rs	30.98	19.38	19.25
	Rct	16.76	4.913	2.649