Supporting Information

Layer Number Dependence of Li⁺ Intercalation on Few-Layer Graphene and Electrochemical Imaging of Its Solid-Electrolyte Interphase Evolution

Jingshu Hui^{†,‡}, Mark Burgess[‡], Jiarui Zhang[‡] and Joaquín Rodríguez-López^{‡,}*

[†]Department of Materials Science and Engineering, University of Illinois at Urbana–Champaign, 1304 West Green Street, Urbana, Illinois 61801, USA

[‡]Department of Chemistry, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, USA

*Corresponding author email address: joaquinr@illinois.edu

Wollaston tip fabrication

Wollaston wire (Goodfellow, Purity 99.9%, 600 nm radius) was sealed in a glass capillary (World Precision Instruments, Sarasota, FL). A 1 cm length of Wollaston Pt wire was placed halfway up a capillary and was chemically etched on the bottom half of the wire to remove the protective layer of silver using a solution of concentrated nitric acid utilizing capillary action to pull the acid solution up the tube. The nitric acid was removed from the capillary using a KimWipe leaving a half chemically etched Wollaston wire in the capillary. The Wollaston wire was then sealed in the glass capillary using a standard method previously described elsewhere.¹ The sealed Wollaston electrode was then sharpened using silicon carbide sandpaper with the aid of an optical microscope. The final RG, radius of glass sheath including the electrode divided by the radius of the electrode, was approximately 25. The large value of RG is uncharacteristic of a typical SECM tip, which will limit the proximity placement of the tip to the substrate, but high resolution SECM images were still able to be collected because extreme closeness to the substrate is not necessary to measure SECM feedback differences.²

1. Rodriguez-Lopez, J.; Shen, M.; Nepomnyashchii, A. B.; Bard, A. J. Scanning Electrochemical Microscopy Study of Ion Annihilation Electrogenenerated Chemiluminescence of Rubrene and $[\text{Ru}(\text{bpy})_3]^{2+}$. *J. Am. Chem. Soc.* 2012, 134, 9240-9250.
2. O'Connell, M. A.; Wain, A. J. Combined electrochemical-topographical imaging: a critical review. *Analytical Methods* 2015, 7, 6983-6999.

Figure S1. Cyclic voltammograms of unpatterned carbon samples. a, Bilayer graphene, insert figure is smaller scale scan after 3 cycles to verify no existence of intercalation peak. b, Four layer graphene. c, HOPG. Test condition: 0.1 M LiBF₄ in 50:50 ratio PC/EC, electrode area was 4.9 mm².

Table S1. Intercalation and de-intercalation peak distributions of 4LG, 6LG and MLG.^a

	4LG	6LG	MLG
Intercalation -- 3	--	0.38-0.27	0.259-0.21
Intercalation -- 2	0.12-0.06	0.25-0.07	0.16-0.13
Intercalation -- 1			0.13-0.06
De-intercalation -- 1	0.17-0.23	0.08-0.19	0.10-0.18
De-intercalation -- 2	0.36-0.44	0.23-0.37	0.18-0.21
De-intercalation -- 3	--	0.39-0.63	0.22-0.26

^a Data were derived from Figure 3c (first cycle), h, and i.

Figure S2. Schematic diagram of 4LG, 6LG and MLG sample structures. Solid-electrolyte interphase (SEI), graphene sheets, SiO_2 wafer substrate, together with the SEI/graphene and graphene/substrate interfaces are indicated in figure.

Calculation of de-intercalation charge in Figure 3 h and i, and theoretical charge for FLG.

Figure S3. Integration baselines of de-intercalation charge for 4LG (a) and 6LG (b). c, crystal structure of LiC_6 – stage 1. Example unit cell for intercalated Li is highlighted with dash lines. Cell constant are labelled in figure. d, Photolithography mask design for etched window for Li ion intercalation.

As discussed in the main text, there are two de-intercalation peaks for 4LG and three for 6LG. The integrating baseline for each peak are indicated in Figure S3 a and b. The integrated charges for each peak are listed as follows:

4LG Peak 1: $3.28 \mu\text{C}$ Peak 2: $8.93 \mu\text{C}$ Total charge: $12.2 \mu\text{C}$

6LG Peak 1: 3.36 μC Peak 2: 1.94 μC Peak 3: 10.4 μC Total charge: 15.7 μC

According to Figure S3 c, one unit cell contains one Li ion, with a size of 0.1574 nm².

Exposed electrode area for FLG samples are 0.048 cm².

Consider about the etched openings (Figure S3 d), 1/64 of graphene area has been removed by photolithography and reactive ion etching procedure. The effective area for FLG sample is 0.04725 cm².

Total number of Li for one layer of stage-1 LiC₆: $0.04725 \text{ cm}^2 / 0.1574 \text{ nm}^2 = 3.002 \times 10^{13}$ atoms.

Total charge of Li for one layer of stage-1 LiC₆: $3.002 \times 10^{13} \text{ atoms} / (6.02 \times 10^{23} \text{ atoms/mol}) * 96485 \text{ C/mol} = 4.81 \mu\text{C}$.

For 4LG, there are at most three layers Li insertion with graphene sheets, then the theoretical intercalation charge is: $4.81 \times 3 = 14.43 \mu\text{C}$. Similarly, the theoretical charge for 6LG is : $4.81 \times 5 = 24.05 \mu\text{C}$.

Compare with experimental data calculated from de-intercalation charge, Li ion filled up to 85 % available sites in 4LG and 65 % available sites in 6LG.

Figure S4. SECM feedback images of N,N,N',N'-tetramethyl p-phenylenediamine (TMPD) after SEI fully formation. Substrate potential: 2.6 V. This image was taken about all Figure 4 d, e and f in main text. The image has no obvious contrast between graphene and etched ionic channel area, which means the SEI remains stable under higher potential. Tip-substrate distance: 133 nm.