Supporting Information

Reduced-Graphene Oxide / Poly(acrylic acid) Aerogels as a Three-Dimensional Replacement for Metal-Foil Current Collectors in Lithium Ion Batteries

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Calculating active material mass percent in the whole electrode

1. As was reported in: H.; Zhang, L.; Pettes, M. T.; Li, H.; Chen, S.; Shi, L.; Piner, R.; Ruoff, R. S. Ultrathin Graphite Foam: A Three-Dimensional Conductive Network for Battery Electrodes. *Nano Lett.* **2012**, 12, 2446–2451.

   Ultrathin Graphene Foam (UGF) density (ρ_{UGF}) = 9.5 mg/cm^3

   LFP areal mass loading (A_{LFP}) = 12 mg/cm^2

   Electrode diameter (D) = 7.6 mm

   Electrode thickness (h) = 1.6 mm

   Particles mass ratio, LFP : Carbon Black : PVDF = 70 : 20 : 10

   Electrode area (A) = $\frac{\pi D^2}{4}$=0.454 cm^2

   Electrode volume (V) = $A \times h$=0.073 cm^3

   Mass of UGF (m_{UGF}) = $\rho_{UGF} \times V$ = 0.690 mg

   Mass of LFP (m_{LFP}) = $A_{LFP} \times A$ = 5.448 mg

   Mass of all particles (m_{total}) = $m_{LFP} \div 0.7$ = 7.783 mg

   LFP mass percent = $\frac{m_{LFP}}{m_{total}+m_{UGF}}$=64%

2. Data obtained from MTI Corporation (bc-af-241lpf-ss, www.mtixtl.com)

   For a 241 mm × 200 mm sheet of conventional Al-foil cathode:

   Al-foil thickness (h_{Al}) = 15 μm = 0.0015 cm

LFP areal mass loading (A_{LFP}) = 120 g/m^2 = 12 mg/cm^2

LFP weight proportion in powder = 91%

Area (A) = 241 mm × 200 mm = 482 cm^2

Al density (ρ_{Al}) = 2700 kg/m^3 = 2700 mg/cm^3

Mass of Al (m_{Al}) = $A \times h_{Al} \times \rho_{Al}$ = 1952.1 mg

Mass of LFP (m_{LFP}) = $A_{LFP} \times A$ = 5784 mg

Mass of all particles (m_{total}) = $m_{LFP} \div 0.91$ = 6356 mg

LFP mass percent = $\frac{m_{LFP}}{m_{total}+m_{Al}}$ = 69.6%

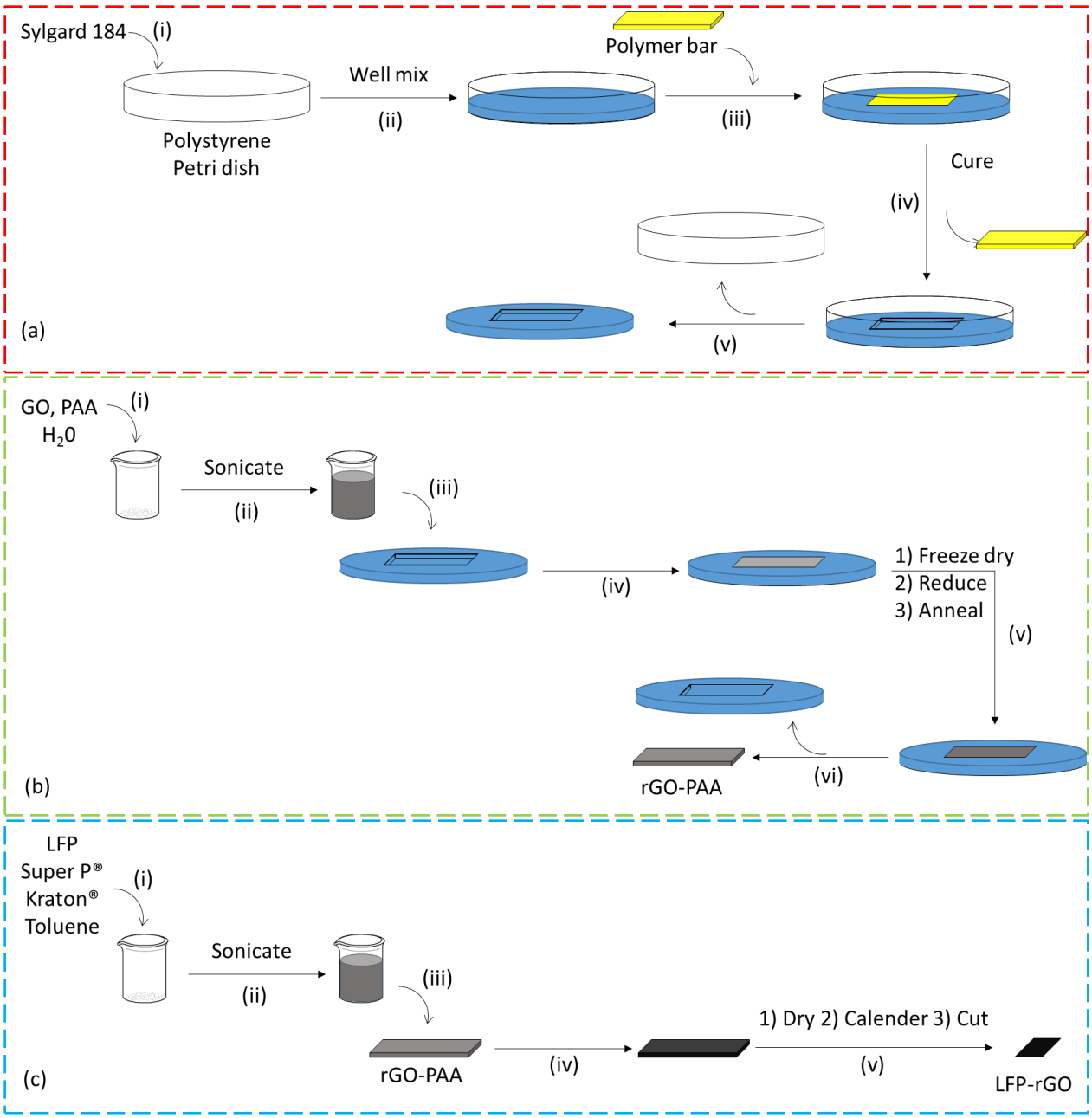

Figure S1. A brief procedure for synthesizing LFP-rGO. (a) Construction of aerogel molds. (i) Add PDMS elastomer and curing agent at recommended 10:1 mass ratio (20 g and 2 g, respectively). (ii) Completely mix by stirring with a stir rod. (iii) Gently place a polymer bar template on top of the elastomer. (iv) Cure the elastomer at 60 ºC for 4 h, then remove the polymer bar. (v) Gently remove the cured PDMS mold from the petri dish. (b) Synthesis of rGO-PAA aerogels. (i) Add water, GO, and PAA (10 mL, 50 mg, and 25 mg, respectively). (ii) Sonicate the

mixture for 10 min to make a homogenously dispersed suspension. (iii) Using a pipette, add the suspension to the PDMS mold made in (a). (iv) Using a pipette, make sure the volume of suspension added is approximately the same as the volume of the mold. (v) Using liquid nitrogen, freeze dry the sample, then pull vacuum for 24 h. Reduce the sample under a HI vapor environment for 24 h. Anneal the sample at 160 ^{o}C for 24 h. (vi) Remove rGO-PAA aerogel from the mold. Properly dispose of the HI exposed mold (solid waste). (c) Construction of LFP-rGO cathodes. (i) Add LFP, Super P®, and Kraton® (1000 mg, 54 mg, and 27 mg, respectively) in a vial containing 15 mL toluene. (ii) Sonicate the mixture for 15 min to obtain a homogenously dispersed suspension. (iii) Slurry-cast the suspension onto the rGO-PAA aerogel bar made in (b). (iv) Let the rGO-PAA aerogel fully absorb the particle suspension. (v) Dry the sample under vacuum at 80^{o}C overnight, compress to the desired thickness using a calender, and cut the sample to the desired size.

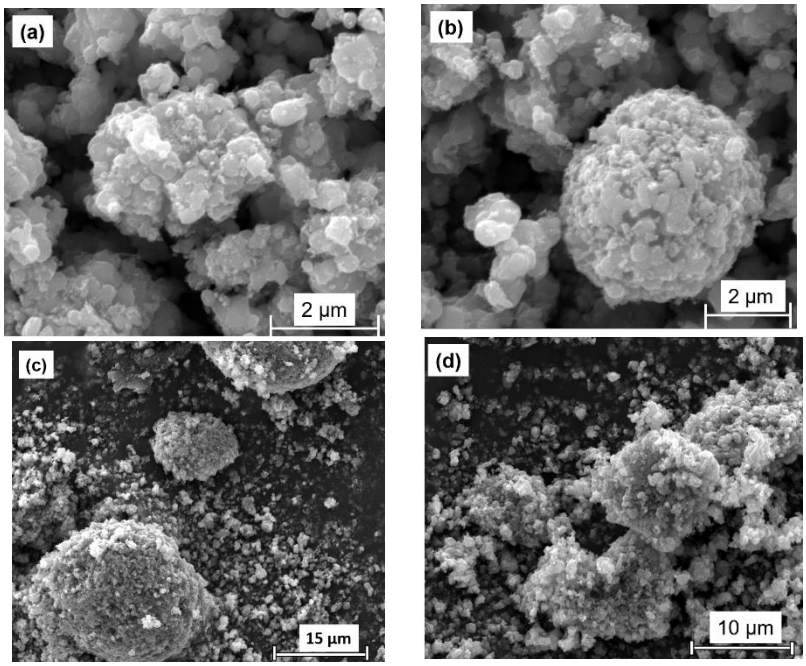

Figure S2. SEM images of commercial LFP particles used in this study demonstrating the large distribution in particle size and morphology at high (a-b) and low (c-d) magnification.

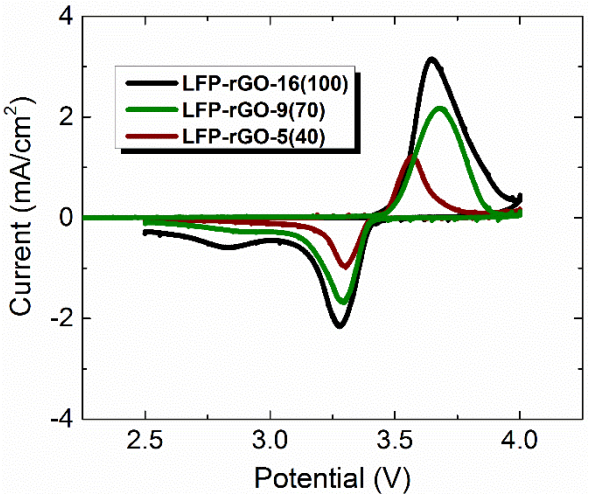

Figure S3. CV traces of LFP-rGO electrodes highlighting the disappearance of the satellite peak at ~ 2.8 V as the thickness and mass loading of the composite LFP-rGO electrodes is decreased.

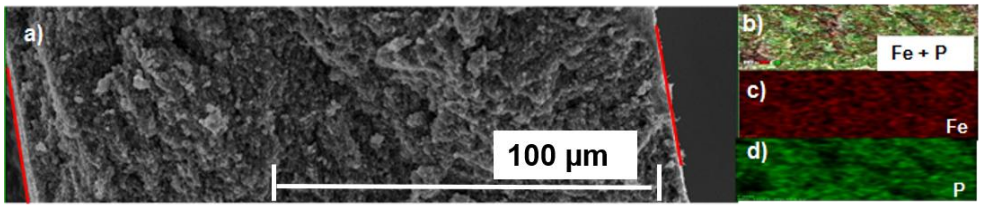

Figure S4. SEM image showing the cross section of an rGO-PAA electrode loaded with 28 mg/cm^2 of LFP and a thickness of ~140 µm. a) SEM image showing effective particle distribution along the cross-section of the rGO-PAA. Red lines indicate surfaces of rGO-PAA. b) Cross sectional EDS of the LFP-rGO electrode. Red is iron and green is phosphorous. c) Iron elemental mapping. d) Phosphorous elemental mapping.

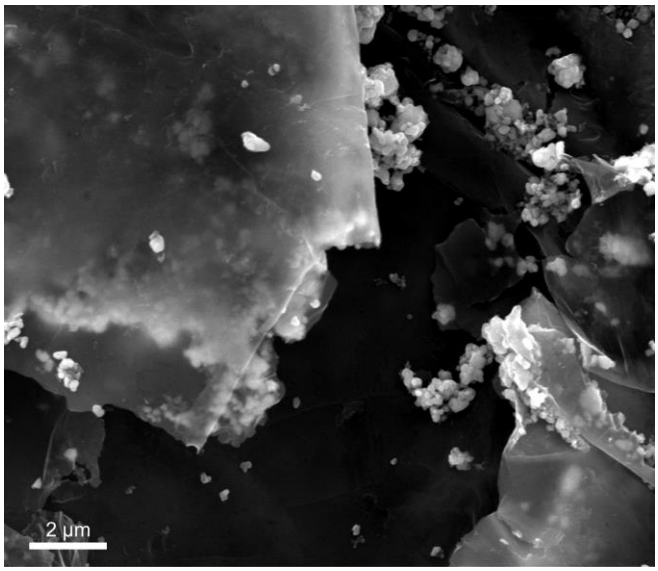

Figure S5. Top-down SEM image of the rGO-PAA electrode after one discharge cycle. Some of the particles were detached from the surface of the electrode during cell-opening. However, after removal of these loose particles from cell-opening, it can be confirmed that that the local film thickness was only a few particles deep on the aerogel surface.

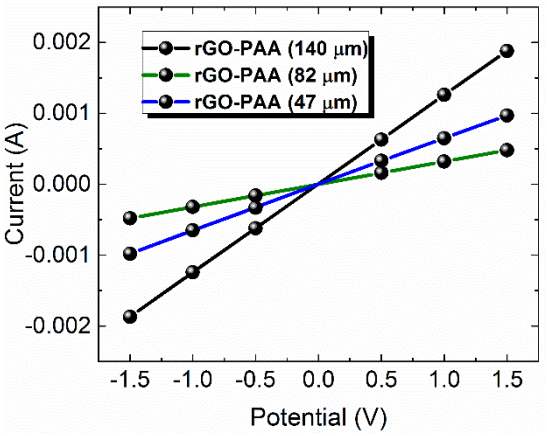

Figure S6. I-V curves obtained from 4-point probe measurements of pristine rGO-PAA (i.e., no LFP added) at different thicknesses.

To determine the electrical conductivity of the rGO-PAA substrate, the sheet resistance of the rGO-PAA was first calculated using the following equation:

$$R_s = \frac{4.53 \times (V_2 - V_1)}{I_2 - I_1} \quad (1)$$

Where R_s is the sheet resistivity (Ω/cm^2), V_2 and V_1 are the voltages (V), and I is the current (A). The sheet resistance was then converted to the bulk resistivity by multiply by the substrate thickness. Taking the reciprocal of bulk resistivity provides the electrical conductivity, which was determined to be $5.3 \times 10^{-2} \pm 3 \times 10^{-2}$ S/m.

Table S1. Selected cell capacities of electrodes with different LFP mass loadings

LFP Mass Loading (mg/cm^2)	9	16	34	73
Electrode density (g/cm^3)	1.4	1.6	1.9	1.7
C/5 Rate (mAh/g)	151	145	139	138
C/2 Rate (mAh/g)	140	118	110	98
1C Rate (mAh/g)	120	83	55	43
2C Rate (mAh/g)	76	36	29	23

Table S2. Summary of experimental values from EIS and CV.

Electrode	LFP-rGO-9(70)	LFP-Al-9(70)	LFP-rGO-16(100)	LFP-Al-16(100)
R_s (Ω)	4.8	13	5.2	19
R_{SEI} (Ω)	209	255	223	296
R_{Li} (Ω)	31	48	35	54
R_{CT1} (Ω	2212	5178	2275	3302
R_{CT2} (Ω)	248	272	495	672
$R_{CTtotal}$ (Ω)	223	258	407	558
Anodic peak current (mA/cm^2)	2.18	1.10	3.13	1.14
Cathodic Peak Current (mA/cm^2)	-1.7	-.65	-2.04	-.89
Peak Separation (mV)	370	490	450	500