Supporting Information

Environmentally Friendly Regeneration of Graphite from Spent Lithium-Ion Batteries for Sustainable Anode Material Reuse

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Table S1: Metal contents of Gr-W and metal recovery rates from Gr-W to various solutions via the three regeneration processes.

Code	Element concentration (mg-metal/g-Gr-W)					
	Al	Co	Cu	Fe	Li	Ni
Gr-W[a]	0.04	0.04	0.36	0.08	3.54	0.01
Gr-AcOH[b]	0.02	0	0.02	0	3.47	0
Gr-KOH[c]	0	0	0.02	0	2.96	0
Gr-N_2[c]	0	0	0	0	0.51	0

a. Metal contents of the Gr-W particles.

b. Metals recovered in the AcOH solution used for lixiviation.

c. Metals recovered in the deionized water used for washing.

ICP-OES sample preparation:

Gr-W (0.2 g) was treated with concentrated nitric acid (HNO_3, 60%, 5 mL) in a microwave oven for 45 min. The solution was then filtered and aqueous nitric acid solution (1%, 1 mL) was added. Subsequently, the solution was diluted to 100 mL with water and analyzed by ICP-OES to quantify the concentration of the metal ions.

Gr-AcOH was prepared by leaching Gr-W with acetic acid, and the solution was separated from the graphite sample by filtration and diluted water to 100 mL. Additionally, nitric acid (HNO_3, 15.7 M, 0.7 mL) was added to the solution for subsequent ICP-OES analysis.

Gr-KOH was prepared by leaching Gr-W with KOH, and the KOH solution was separated from the graphite sample by filtration. After heating the graphite sample at 800 °C under N_2 flow, deionized water (100 mL) was added, stirred, and filtrated, and the filtrate was neutralized with nitric acid (HNO_3, 3 mL) and then diluted with water to 100 mL. Additionally, 0.7 mL of 15.7 M HNO_3 (0.7 mL, 15.7 M) was added to the solution to enable the quantification of metal concentrations via ICP-OES.

Gr-N_2 was prepared by heating Gr-W at 800 °C under N_2 flow. Water (3 mL) was added to Gr-N_2 to dissolve lithium present in the graphite sample, and the mixture was filtered. Subsequently, the filtrate was diluted with water to 100 mL, and HNO_3 (0.7 mL, 15.7 M) was subsequently added to prepare the solution for ICP-OES.

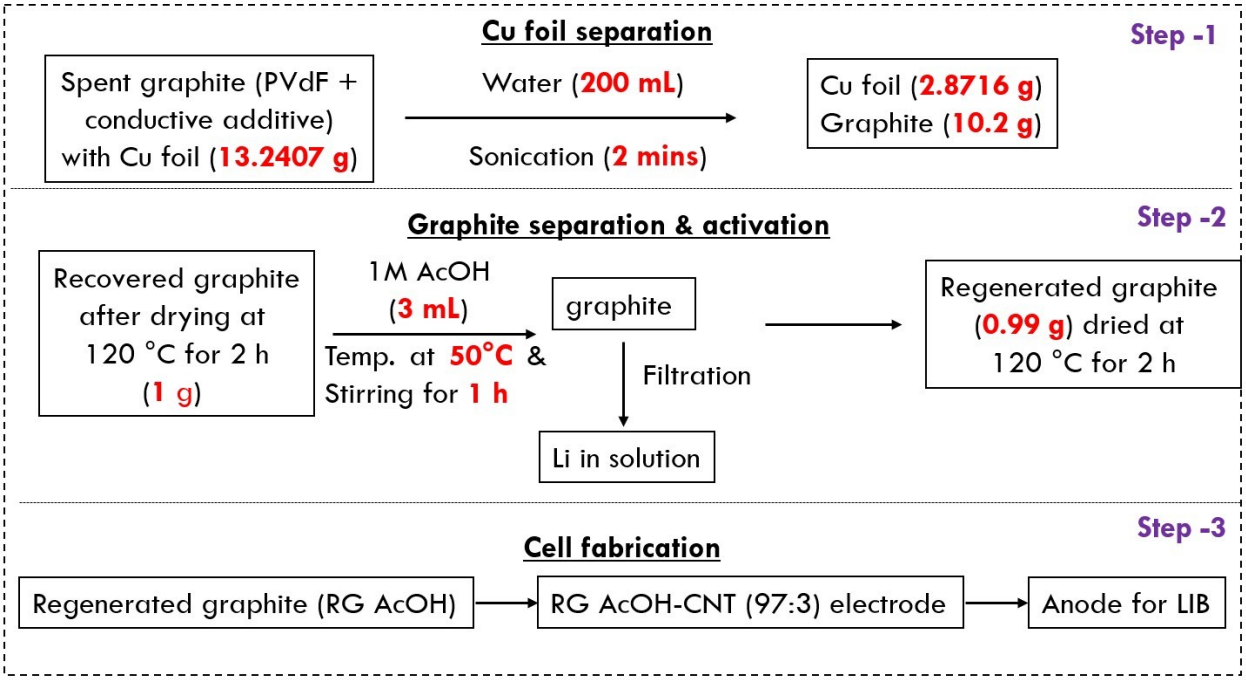

Figure S1: Flow chart for graphite regeneration by the acid lixiviation process (Gr-AcOH).

Energy Consumption of the acid lixiviation (Gr-AcOH) process

Heating

Hot plate at 50 °C for 1 h = 0.01 kWh kg_{gr}^{-1} (actual power)

Drying:

120 °C for 2 h = 0.34 kWh kg_{gr}^{-1} (actual power)

Total energy consumption = 0.01 kWh kg_{gr}^{-1} + 0.34 kWh kg_{gr}^{-1}

Total energy consumption = 0.351 kW.h kg_{gr}^{-1}

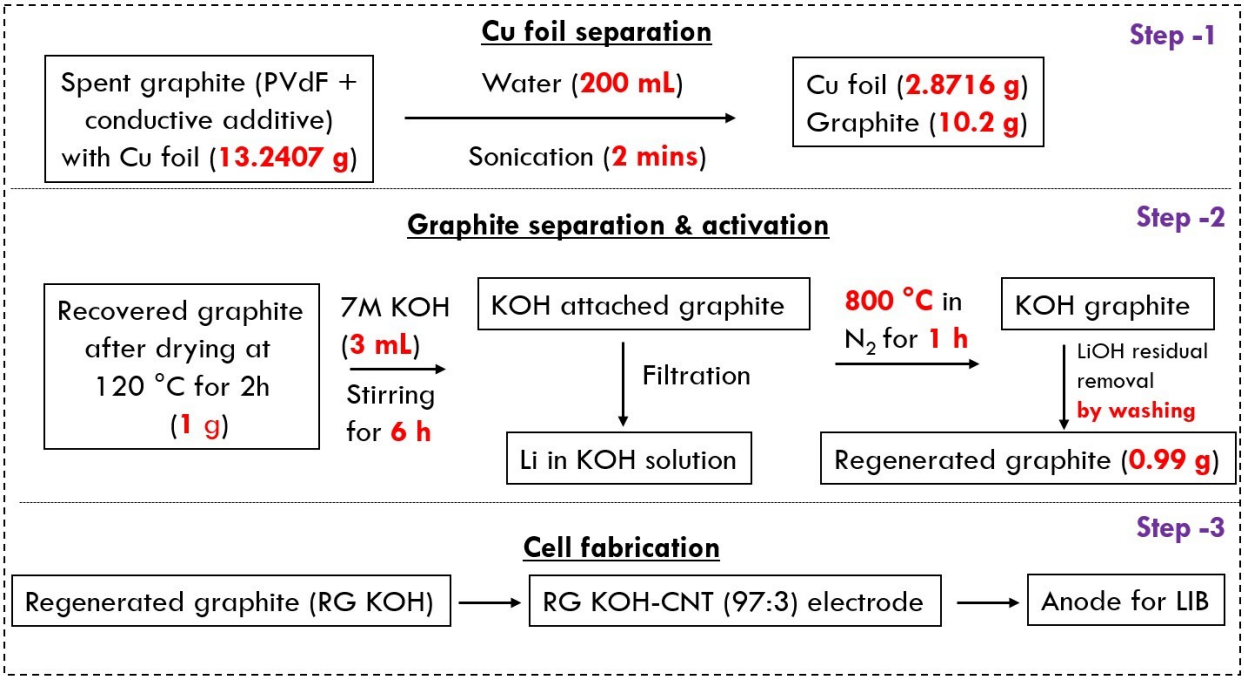

Figure S2: Flow chart of graphite regeneration by the alkali lixiviation technique (Gr-KOH) followed by heat treatment.

Energy Consumption of the alkali lixiviation process followed by heat treatment (Gr-KOH)

Stirring:

Stirring for 6 h = 0.01 kW.h kg_{gr}^{-1} (actual power)

Drying:

120 °C for 2 h (using 1 g graphite) = 0.34 kW.h kg_{gr}^{-1} (actual power)

Annealing:

Annealed at 800 °C for 1 h (using 1 g of sample) = 0.57 kWh kg_{gr}^{-1} (actual power)

Total energy consumption = 0.34 kW h kg_{gr}^{-1} + 0.57 kWh kg_{gr}^{-1}

Total energy consumption = 0.91 kWh kg_{gr}^{-1}

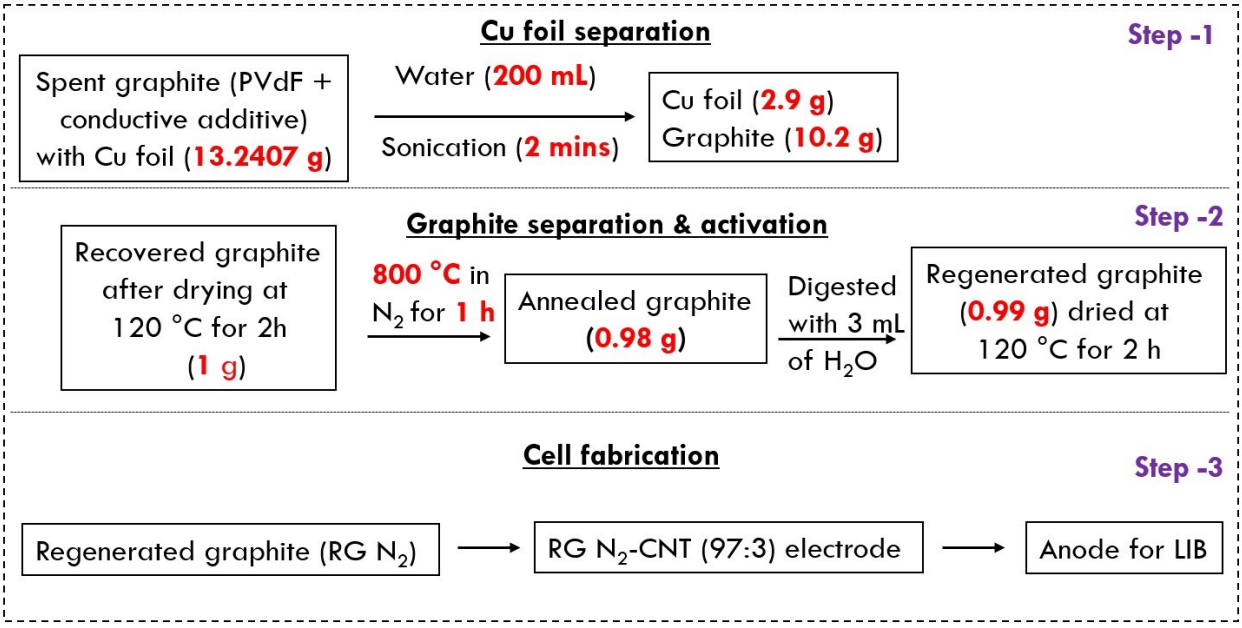

Figure S3: Flow chart of graphite regeneration by gas treatment with annealing (Gr-N_2) followed by lixiviation.

Energy Consumption of thermal treatment under N_2 followed by lixiviation (Gr-N_2)

Drying:

120 °C for 2 h (using 1 g graphite) = 0.34 kWh kg_{gr}^{-1} (actual power)

Annealing:

Annealed at 800 °C for 1 h (using 1 g graphite) = 0.57 kWh kg_{gr}^{-1} (actual power)

Total energy consumption = 0.34 kW h kg_{gr}^{-1} + 0.57 kWh kg_{gr}^{-1}

Total energy consumption = 0.91 kWh kg_{gr}^{-1}

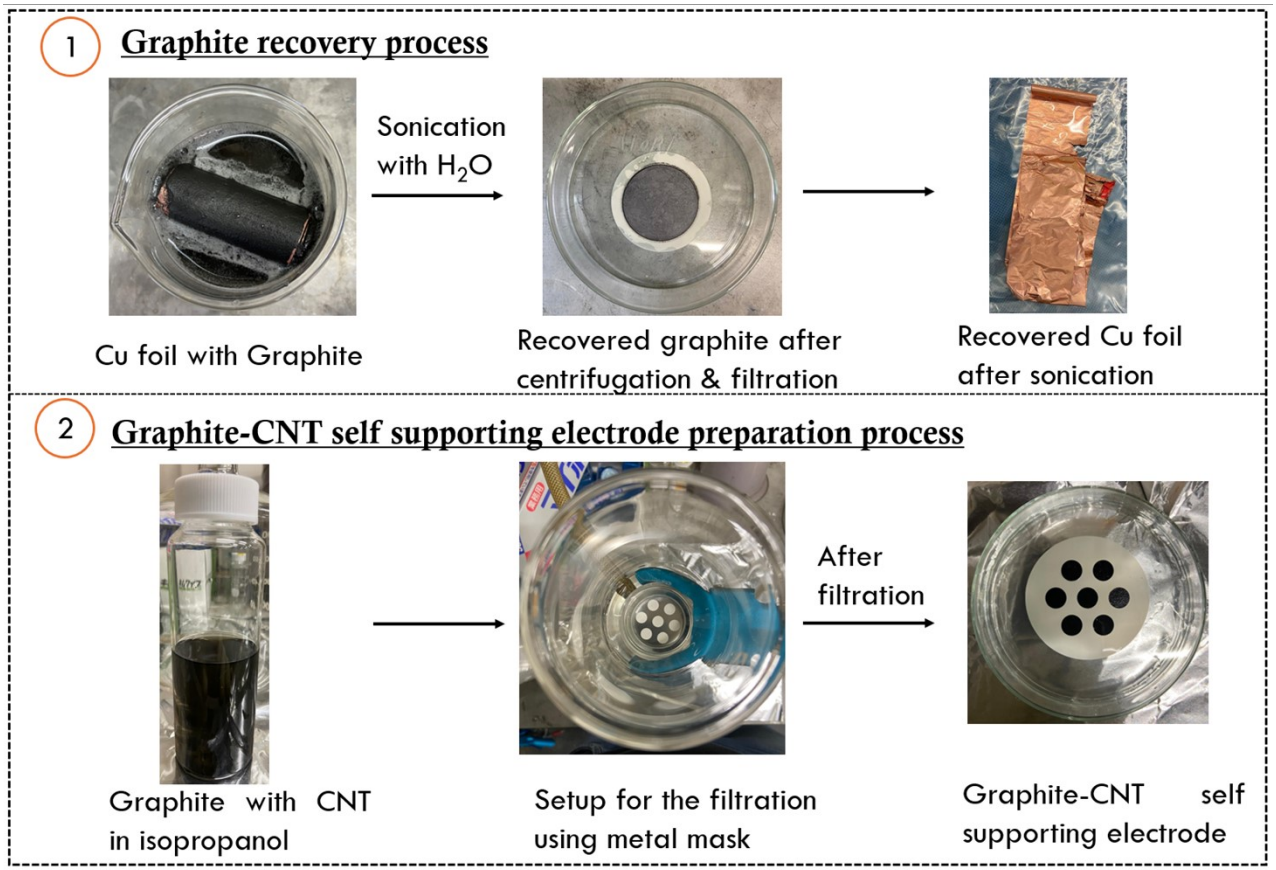

Figure S4: Photos illustrating the recovery of spent graphite from copper foil and the preparation of graphite-CNT self-supporting electrodes.

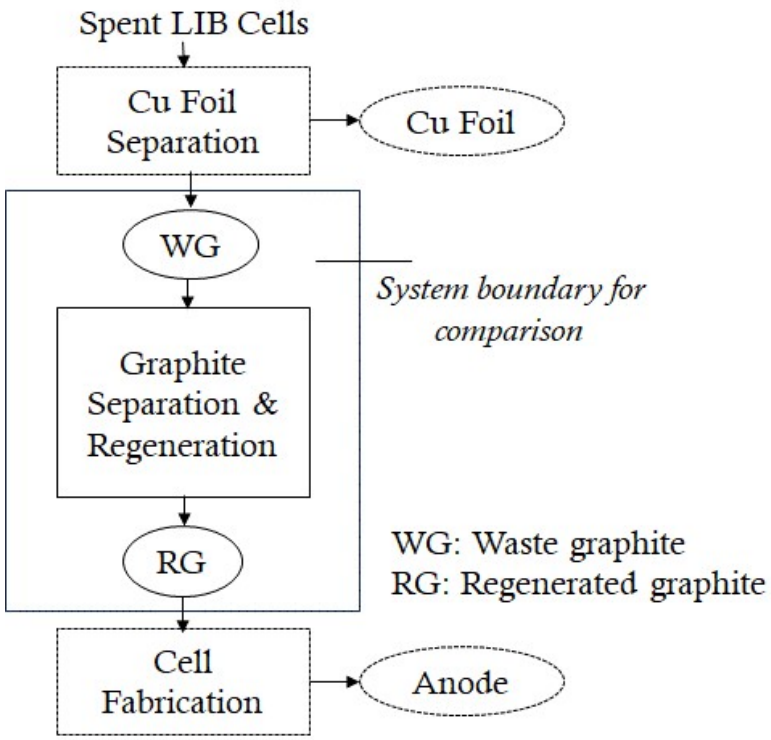

Figure S5. Gate-to-gate system boundary for comparing the environmental performance of graphite separation and activation alternatives in this study (dotted shapes are not included).

Table S2. Energy consumption of the laboratory-scale energy processing of 1 g graphite (unit: $kWh_{electricity}$/1-g-graphite)

		Lab-actual [1]	Lab-ideal [2]	Lab equipment
Gr-AcOH	Heating & stirring	0.02	2.00E-04	C-MAG HS 7 digital -IKA (heating temperature range = 50 – 500 ºC; stirring capacity up to 10 L; stirring speed range = 100 – 1500 rpm)
	Drying	0.17	9.91E-05 [3]	AXEL GLOBAL AVO-200 SB (inner capacity upto 8 L; temperature range = 40 – 220 ºC; heater capacity = 800 W)
Gr-KOH	Stirring	0.01	1.00E-04	C-MAG HS 7 digital -IKA (heating temperature range = 50 – 500 ºC; stirring capacity up to 10 L; stirring speed range = 100 – 1500 rpm)
	Annealing	0.57	1.37E-03	Asahi Rikagaku ARF-50K ceramic electric tubular reactor openable 700 W; Furnace diameter = φ51 mm; Maximum temperature = 1200 ºC
	Drying	0.17	9.91E-05	AXEL GLOBAL AVO-200 SB (inner capacity upto 8 L; temperature range = 40 – 220 ºC; heater capacity = 800 W)
Gr-N_2	Annealing	0.57	1.37E-03	Asahi Rikagaku ARF-50K ceramic electric tubular reactor openable 700 W; Furnace diameter = φ51 mm; Maximum temperature = 1200 ºC
	Drying	0.17	9.91E-05	AXEL GLOBAL AVO-200 SB (inner capacity upto 8 L; temperature range = 40 – 220 ºC; heater capacity = 800 W)

[1] Lab-actual is the electricity consumed in actual experiment measured using a clamp meter in a laboratory environment. Overestimation occurred because this is a batch process and the full capacity of the equipment is not used.

[2]Lab-ideal is estimated by normalizing electricity from "lab-actual" with ½ of the maximum treatment capacity of the equipment per batch.[35]

[3] Estimated based on the heat capacity and heat of water vaporization. A 10% water content in graphite and a 100 K temperature increase were assumed.

Table S3. Energy consumption of estimated pilot-scale processing of 100 kg graphite (unit: $kWh_{electricity}$/100-kg-graphite).

		Pilot	Pilot-scale equipment
Gr-AcOH	Heating & stirring	0.673	Sepro® leach reactor, SRL250 model for volumes up to 0.5 m^3; 3.7 kW [35]
	Drying[1]	8.404	BioLab® convection oven, PF 200 model for volumes up to 230 L; maximum temperature 300ºC; 2.7 kW[35]
Gr-KOH	Stirring	4.036	Sepro® leach reactor, SRL250 model for volumes up to 0.5 m^3; 3.7 kW [35]
	Annealing	18.809	BioLab® modified atmosphere chamber furnace, GPCMA/174 model for volumes up to 174 L; 36 kW [35]
	Drying	8.404	BioLab® convection oven, PF 200 model for volumes up to 230 L; maximum temperature 300ºC; 2.7 kW [35]
Gr-N_2	Annealing	18.809	BioLab® modified atmosphere chamber furnace, GPCMA/245 model for volumes up to 245 L; 45 kW [35]
	Drying	8.404	BioLab® convection oven, PF 200 model for volumes up to 230 L; maximum temperature 300ºC; 2.7 kW[35]

[1]The energy consumption for drying is calculated as follows:

The energy consumption of facility operation is:

2.7 kW * 2 hr * (100 kg-graphite/2200 kg m^{-3}) / (0.23 m^3 reactor capacity * ½ max allowed) = 2.134 kWh

The energy consumption of the vaporization of 10 kg of water from 100 kg of graphite was calculated as

2257 J/g * 10 kg = 6.270 kWh.

The total energy consumption was therefore 2.134 kWh + 6.270 kWh = 8.404 kWh.

Table S4. Materials used in processing 1 kg graphite.

		Amount (kg)	Reference process from Ecoinvent
Gr-AcOH	Acetic acid	0.18	Market for acetic acid, without water, in 98% solution state | acetic acid, without water, in 98% solution state | Cutoff, U, GLO
	Deionized water	19.00	Market for water, deionised | water, deionised | Cutoff, U, RoW
Gr-KOH	KOH	1.18	Market for potassium hydroxide | potassium hydroxide | Cutoff, U, GLO
	Deionized water	19.10	Market for water, deionised | water, deionised | Cutoff, U, RoW
	Nitrogen gas	0.15	Market for nitrogen, liquid | nitrogen, liquid | Cutoff, U, RoW
Gr-N_2	Deionized water	3.00	Market for water, deionised | water, deionised | Cutoff, U, RoW
	Nitrogen gas	0.15	Market for nitrogen, liquid | nitrogen, liquid | Cutoff, U, RoW

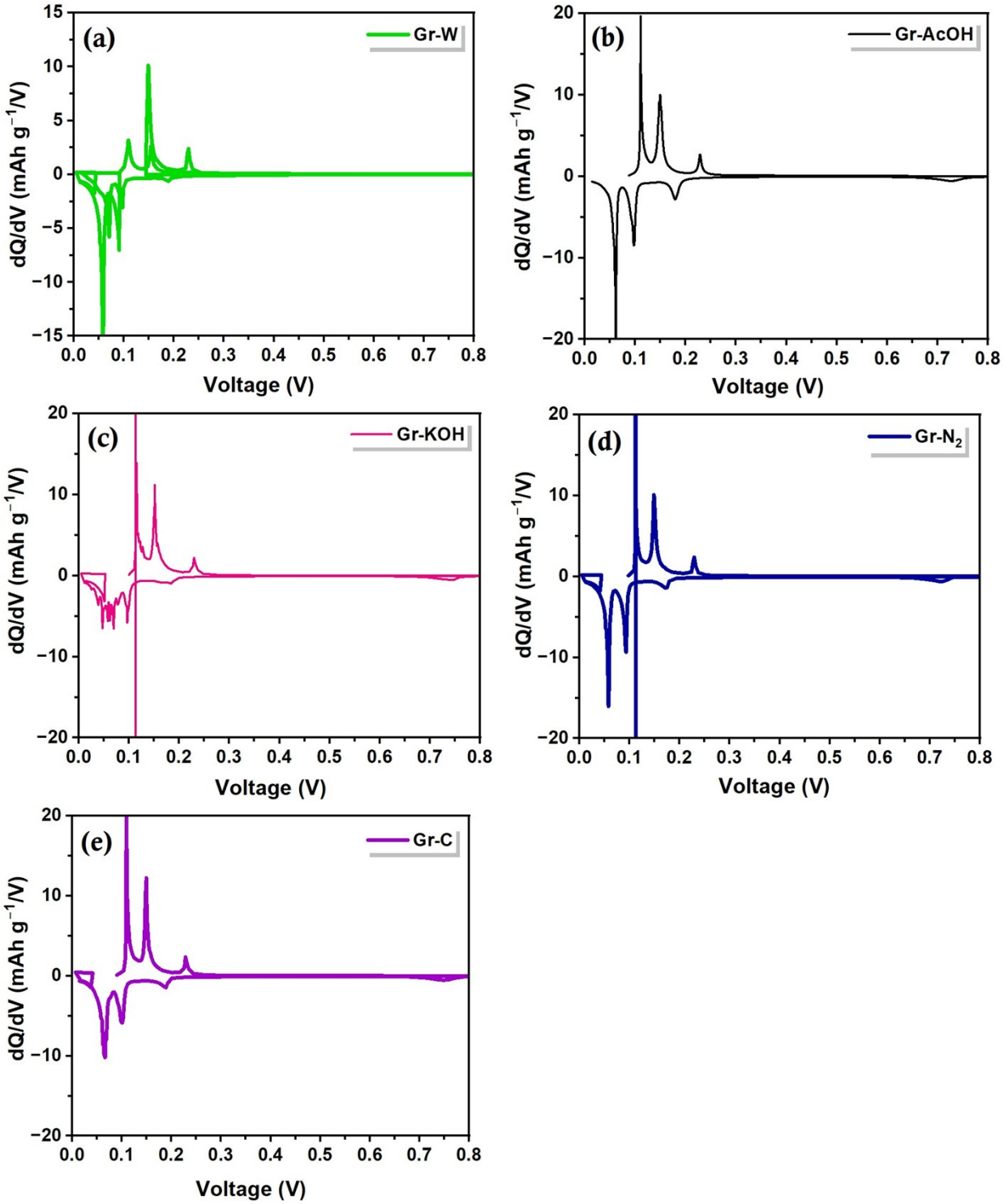

Figure S6: dq/dV analysis of the graphite half-cells (CNT-based electrodes). (a) Gr-W, (b) Gr-AcOH, (c) Gr-KOH, (d) Gr-N_2, (e) Gr-C.

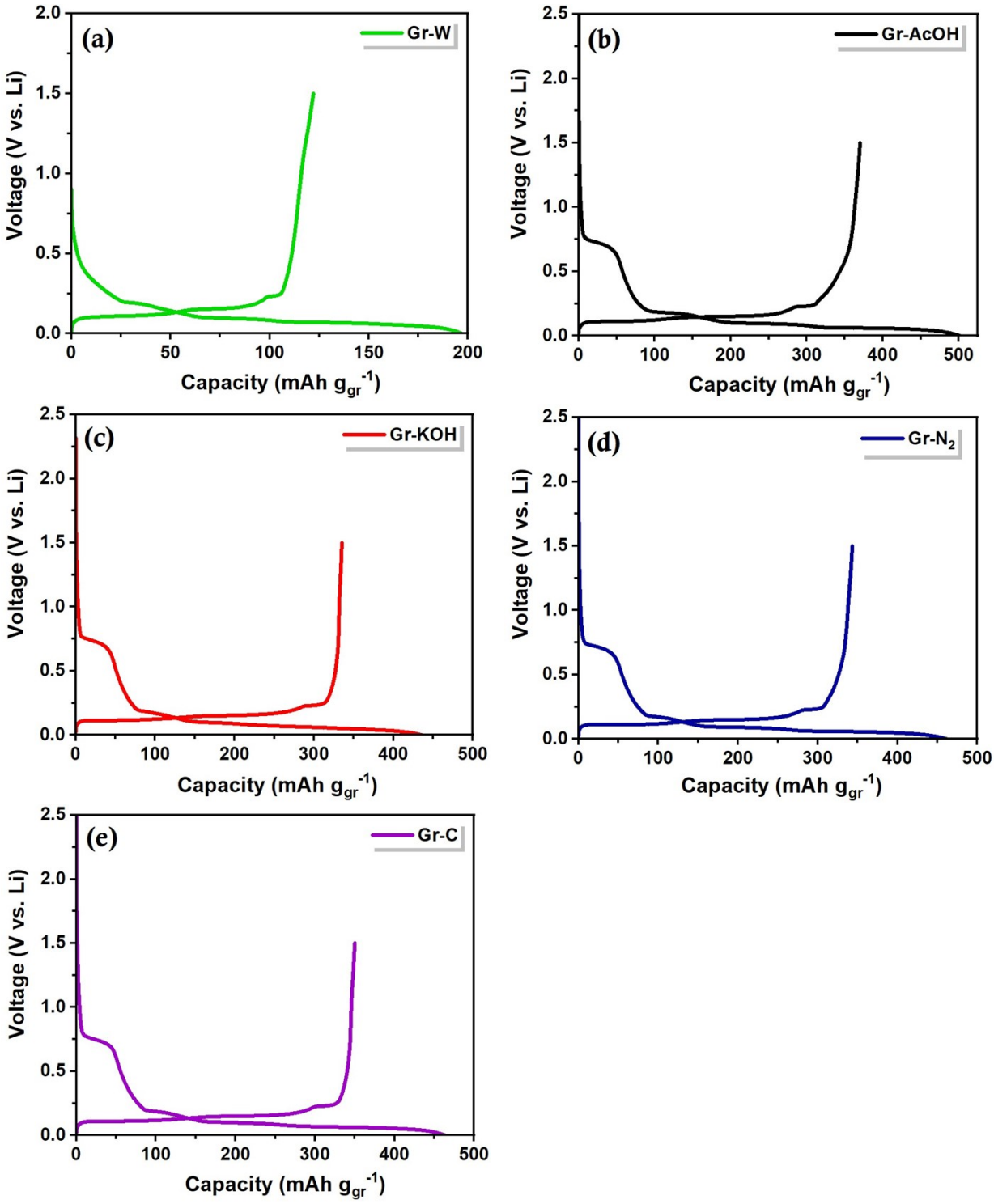

Figure S7: Initial lithiation-delithiation curves of the graphite half-cells (CNT-based electrodes). (a) Gr-W, (b) Gr-AcOH, (c) Gr-KOH, (d) Gr-N_2, (e) Gr-C.

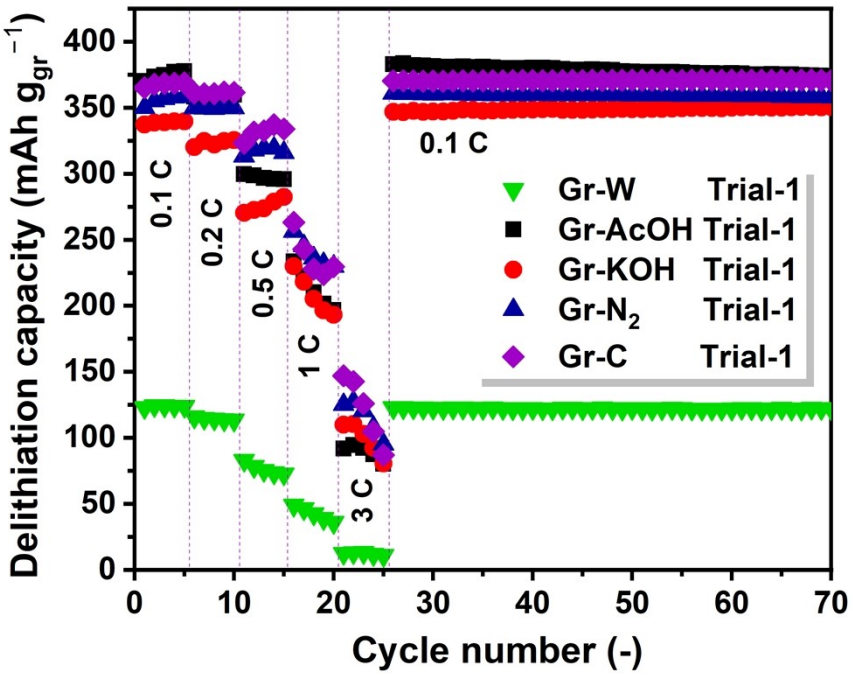

Figure S8: Repeatability of the rate performance of all graphite samples (CNT-based electrodes).

- **Gr-W average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 123.8, 114.3, 76.4, 42.4 & 12.1 mAh g_{gr}^{-1}, respectively**
- **Gr-AcOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C,1C & 3 C= 374.6, 359.1, 297.3, 212.8 & 89.2 mAh g_{gr}^{-1}, respectively**
- **Gr-KOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 338.8, 323.4, 275.5, 208.6 & 99.2 mAh g_{gr}^{-1}, respectively**
- **Gr-N_2 average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 355.7, 350, 317.1, 240, & 115.1 mAh g_{gr}^{-1}, respectively**
- **Gr-C average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 367.7, 361.2, 331.6, 237.4 & 121.5 mAh g_{gr}^{-1}, respectively**

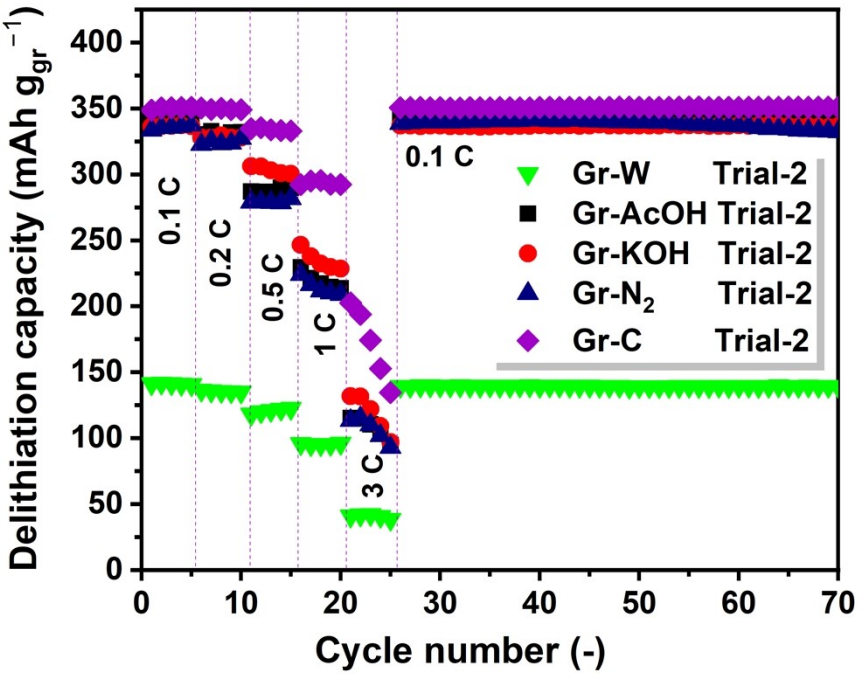

Figure S9: Repeatability of the rate performance of all graphite samples (CNT-based electrodes).

- **Gr-W average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 141.1, 135.4, 120.6, 95.3 & 40.7 mAh g_{gr}^{-1}, respectively**
- **Gr-AcOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C,1C & 3 C= 352.1, 341.4, 288.1, 219.3 & 107.8 mAh g_{gr}^{-1}, respectively**
- **Gr-KOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 336.7, 328.4, 303.6, 235 & 118.3 mAh g_{gr}^{-1}, respectively**
- **Gr-N_2 average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 335.7, 324.5, 279.4, 214.3 & 106.8 mAh g_{gr}^{-1}, respectively**
- **Gr-C average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 350.3, 349.6, 334.0, 293.5, & 171.7 mAh g_{gr}^{-1}, respectively**

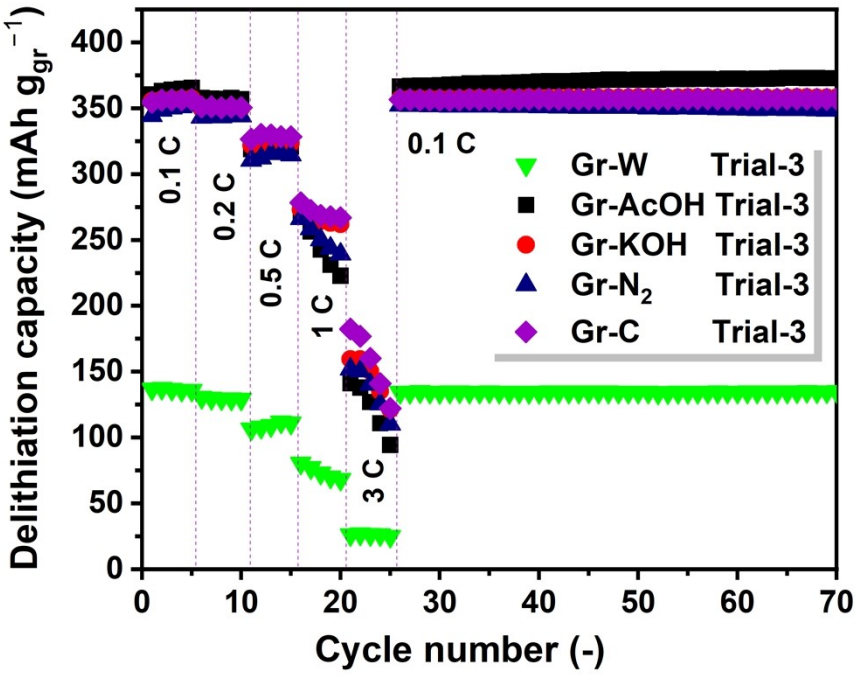

Figure S10: Repeatability of the rate performance of all graphite samples (CNT-based electrodes).

- **Gr-W average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 136.4, 129.5, 109.2, 73.7, 26.0 mAh g_{gr}^{-1}, respectively**
- **Gr-AcOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C,1C & 3 C= 363.6, 357.4, 321.6, 244.4, 122.2 mAh g_{gr}^{-1}, respectively**
- **Gr-KOH average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 356.7, 349.8, 323.7, 266, 145.1 mAh g_{gr}^{-1}, respectively**
- **Gr-N_2 average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 349.2, 343.9, 313.6, 251.6, 135.6 mAh g_{gr}^{-1}, respectively**
- **Gr-C average delithiation capacities at 0.1C, 0.2 C, 0.5 C, 1C & 3 C = 356.0, 350.9, 328.6, 270.7, 156.4 mAh g_{gr}^{-1}, respectively**

Table S5. Comparison of the rate performance of all three Gr-W graphite coin cells at each rate

Rate	Gr-W 1st coin cell (mA h g_{gr}^{-1})	Gr-W 2nd coin cell (mA h g_{gr}^{-1})	Gr-W 3rd coin cell (mA h g_{gr}^{-1})
0.1 C	123.8	141.1	136.4
0.2 C	114.3	135.4	129.5
0.5 C	76.4	120.6	109.2
1 C	42.4	95.3	73.7
3 C	12.1	40.7	26.0

***Average capacities of all cells were calculated from five cycles at each rate.**

Table S6. Comparison of the rate performance of all three Gr-AcOH graphite coin cells at each rate.

Rate	Gr-AcOH 1st cell (mA h g_{gr}^{-1})	Gr-AcOH 2nd cell (mA h g_{gr}^{-1})	Gr-AcOH 3rd cell (mA h g_{gr}^{-1})
0.1 C	374.6	352.1	363.6
0.2 C	359.1	341.4	357.4
0.5 C	297.3	288.1	321.6
1 C	212.8	219.3	244.4
3 C	89.2	107.8	122.2

***Average capacities of all cells were calculated from five cycles at each rate.**

Table S7. Comparison of the rate performance of all three Gr-KOH graphite coin cells at each rate.

Rate	Gr-KOH 1st cell (mA h g_{gr}^{-1})	Gr-KOH 2nd cell (mA h g_{gr}^{-1})	Gr-KOH 3rd cell (mA h g_{gr}^{-1})
0.1 C	338.8	336.7	356.7
0.2 C	323.4	328.4	349.8
0.5 C	275.5	303.6	323.7
1 C	208.6	235	266
3 C	99.2	118.3	145.1

***Average capacities of all cells were calculated from five cycles at each rate.**

Table S8. Comparison of the rate performance of all three Gr-N_2 graphite coin cells at each rate

Rate	Gr-N_2 1st coin cell (mA h g_{gr}^{-1})	Gr-N_2 2nd coin cell (mA h g_{gr}^{-1})	Gr-N_2 3rd coin cell (mA h g_{gr}^{-1})
0.1 C	355.7	335.7	349.2
0.2 C	350.0	324.5	343.9
0.5 C	317.1	279.4	313.6
1 C	240.0	214.3	251.6
3 C	115.1	106.8	135.6

***Average capacities of all cells were calculated from five cycles at each rate.**

Table S9. Comparison of the rate performance of all three Gr-C graphite coin cells at each rate

Rate	Gr-C 1st coin cell (mA h g_{gr}^{-1})	Gr-C 2nd coin cell (mA h g_{gr}^{-1})	Gr-C 3rd coin cell (mA h g_{gr}^{-1})
0.1 C	367.7	350.3	356.0
0.2 C	361.2	349.6	350.9
0.5 C	331.6	334.0	328.6
1 C	237.4	293.5	270.7
3 C	121.5	171.7	156.4

***Average capacities of all cells were calculated from five cycles at each rate.**

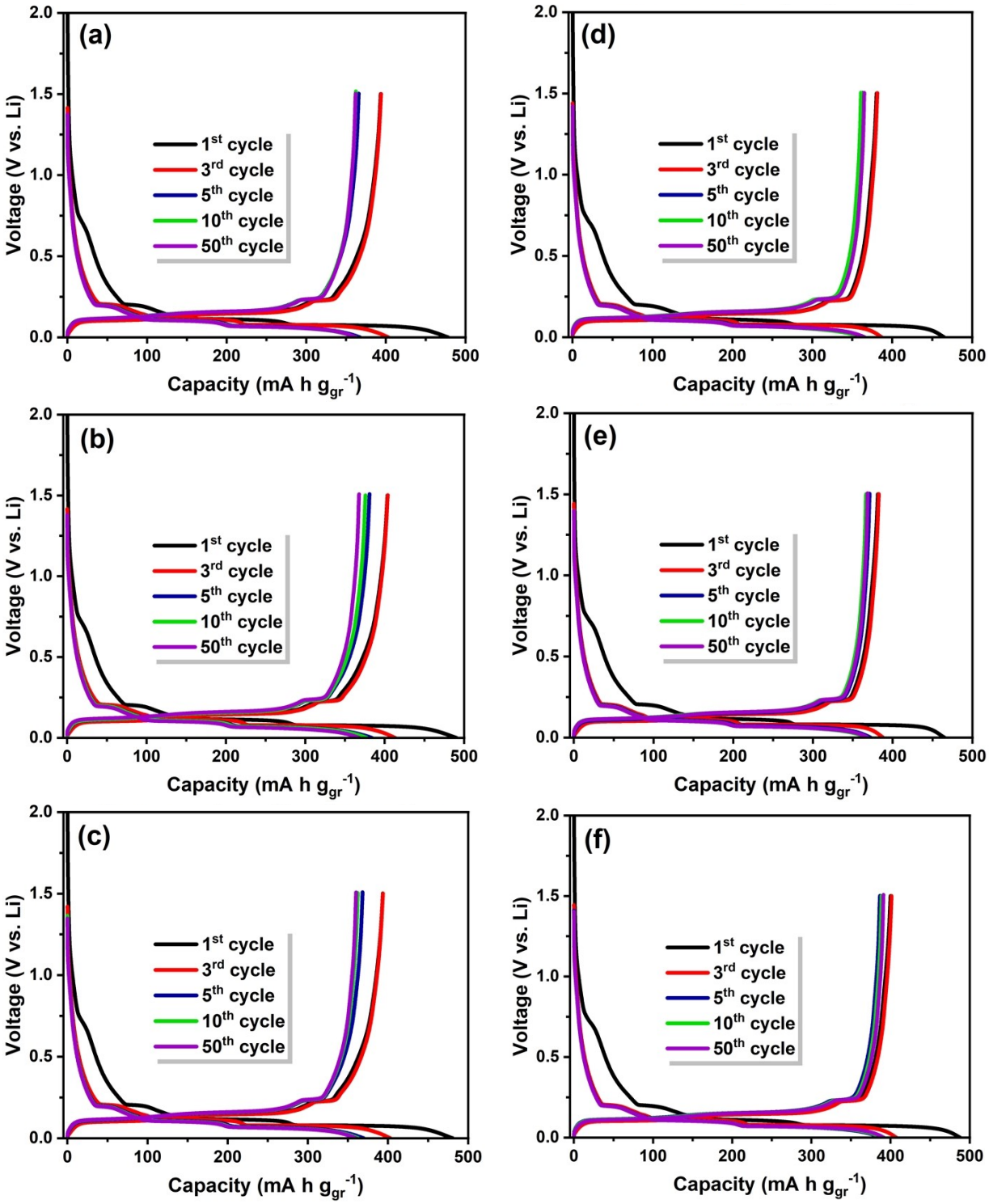

Figure S11: Lithiation-delithiation curves of the graphite half-cells (slurry-based electrodes). (a) Gr-N_2_cell-1, (b) Gr-N_2_cell-2, (c) Gr-N_2_cell-3, (d) Gr-C_cell-1, (e) Gr-C_cell-2, (f) Gr-C_cell-3.

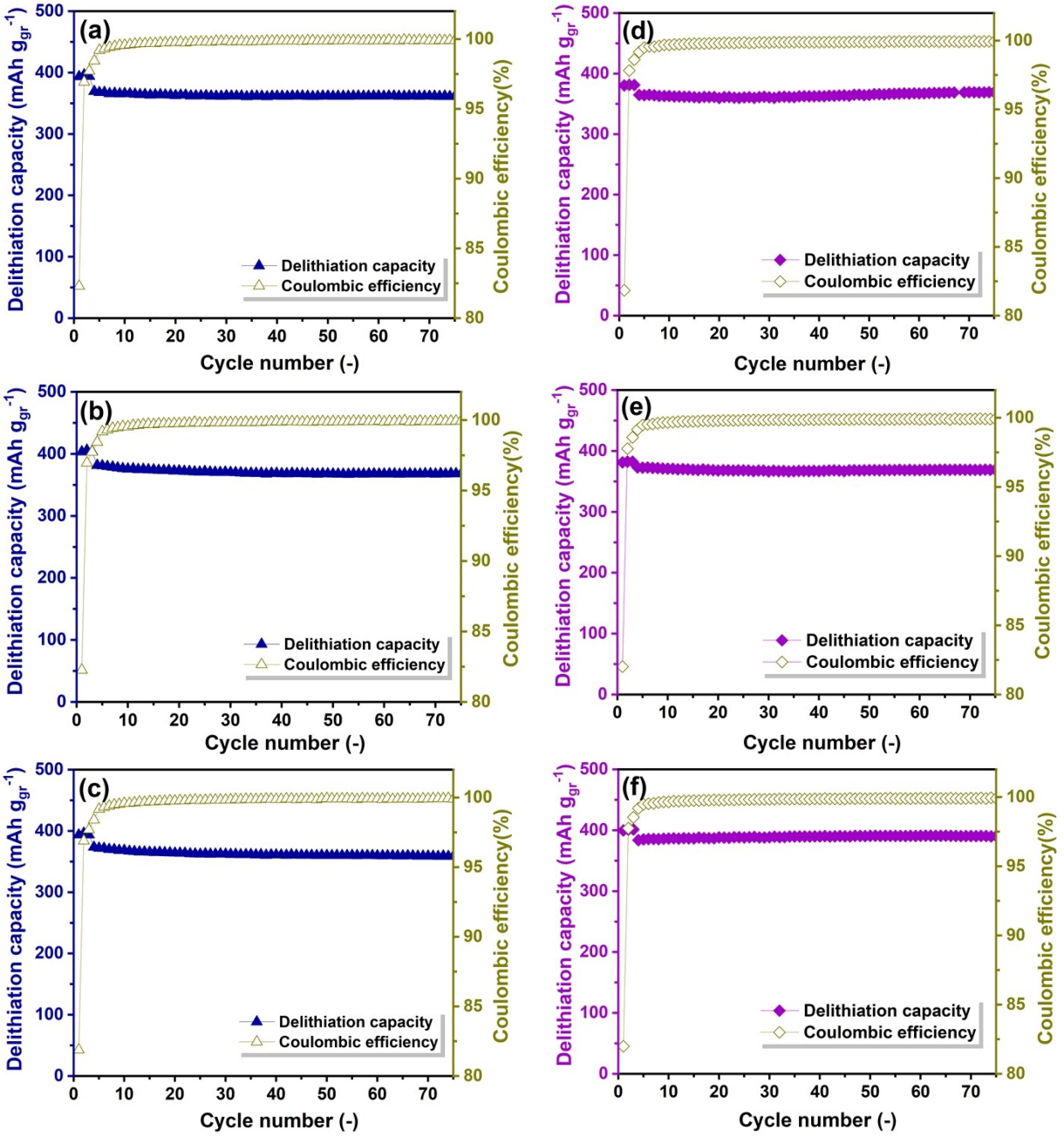

Figure S12: Cycling performance of the graphite half-cells (slurry-based electrodes). (a) Gr-N_2_cell-1, (b) Gr-N_2_cell-2, (c) Gr-N_2_cell-3, (d) Gr-C_cell-1, (e) Gr-C_cell-2, (f) Gr-C_cell-3.

Table S10: Comparison of Regeneration Methods, Energy Consumption, Environmental Impact (Carbon Footprint), and Electrochemical Performance (Capacity and Cycle Retention) of Graphite Electrodes. Initial delithiation capacity and cycle performance show the average values of three cells for each treatment.

Sample code	**Regeneration method**	**Regeneration conditions**	**Energy consumption ($kWh_{electricity}$/ 100-kg-graphite)**	**Environmental impact ($kgCO_2e/kg_{graphite}$)**	**Initial delithiation capacity (mAh g_{gr}^{-1}) & Coulombic efficiency (%)**	**Cycle performance (75^{th} cycle capacity (mAh g_{gr}^{-1}) & capacity retention (%))**
CNT-based electrode fabrication method						
Gr-W	-	-	-	-	122 & 61.9	128 & 105.2
Gr-AcOH	Acid treatment by organic acid	1 g of spent graphite + 3 mL of 1 M CH_3COOH at 50 °C for 1 h with stirring	9.1 (for heating + stirring & drying)	0.49	370 & 73.7	346 & 93.4
Gr-KOH	Alkali treatment followed by annealing	1 g of spent graphite + 3 mL of 7 M KOH with stirring at room temperature for 6 h followed by an annealing at 800 °C under N_2 (1 L/min) for 1 h	31.2 (for stirring, annealing & drying)	3.53	335 & 76.9	332 & 99.1
Gr-N_2	Gas treatment under annealing	1 g of spent graphite annealed at 800 °C for 1 h under N_2 (1 L/min) followed by digested with 3 mL of deionized water	27.2 (for annealing and drying)	0.27	343 & 74.3	343 & 100
Gr-C	Commercial graphite	N/A	N/A	N/A	350 & 75.5	350 & 99.9
Slurry-based electrode fabrication method						
Gr-N_2	Gas treatment under annealing	1 g of spent graphite annealed at 800 °C for 1 h under N_2 (1 L/min) followed by digested with 3 mL of deionized water	27.2 (for annealing and drying)	0.27	397 & 82	363 & 91.4
Gr-C	Commercial graphite	N/A	N/A	N/A	387 & 82	376 & 97

Table S11. Contribution analysis of the global warming potential (GWP) of graphite recovery with the three methods at laboratory and pilot scales (unit: $kgCO_2e/kg$-graphite).

		lab-actual [1]	lab-ideal [2]	pilot
Gr-AcOH	acetic acid	0.418	0.418	0.418
	deionized water	0.009	0.009	0.009
	electricity	137.491	0.216	0.066
	TOTAL	**137.919**	**0.644**	**0.493**
Gr-KOH	KOH	3.230	3.230	3.230
	deionized water	0.009	0.009	0.009
	nitrogen gas	0.067	0.067	0.067
	electricity	542.729	3.230	0.226
	TOTAL	**546.035**	**4.445**	**3.533**
Gr-N_2	deionized water	0.001	0.001	0.001
	nitrogen gas	0.067	0.0067	0.067
	electricity	535.492	1.067	0.197
	TOTAL	**535.561**	**1.135**	**0.266**

[1] the electricity requirement for laboratory equipment was measured without considering the maximum treatment capacity; overestimation was expected.

[2] the electricity requirement for laboratory equipment was calculated considering the treatment capacity (Table S7).

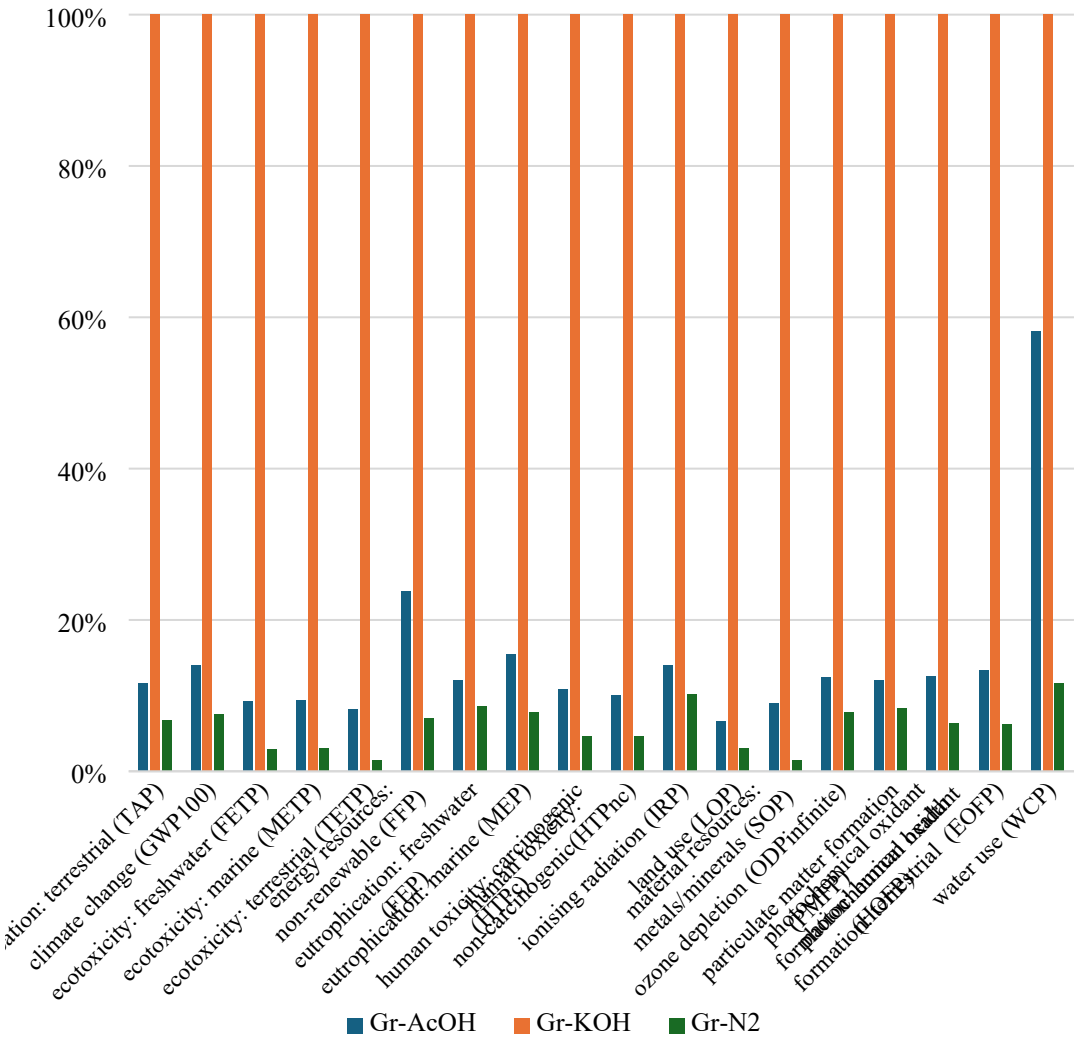

Figure S13. Comparison of all environmental indicators in ReCiPe 2016 LCIA methods on the pilot-scale of the three recycling methods. The result is normalized against Gr-KOH for easier comparison as Gr-AcOH and Gr-N_2 are lower than Gr-KOH.