

Supporting Information

Recovery of graphite from industrial lithium-ion battery black mass

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Supplementary Methods: One-step Leaching of Black Mass

The black mass was leached with H_2SO_4 , with adding H_2O_2 , to extract high-value cathode materials and purify graphite. After leaching, the solid residue was filtrated, sieved, and dried. The resulting powder was designated as recovered graphite. All leaching processes were conducted using a 2 M acid concentration with a solid-liquid ratio of 50 g L^{-1} at $90 \text{ }^\circ\text{C}$ for 6 hours, with the addition of 1.5% (v/v) H_2O_2 (30% w/w) as a reducing agent.

Table S1: ICP-MS result of black mass

Element	Li	Co	Ni	Mn	Fe	P	Al	Cu
Batch 1 (wt.%)	3.45%	2.25%	8.32%	22.29%	0.69%	1.58%	3.62%	11.14%
Batch 2 (wt.%)	1.69%	1.24%	4.41%	10.26%	0.37%	1.00%	5.03%	5.54%
Batch 3 (wt.%)	2.46%	1.85%	6.56%	15.30%	0.65%	1.43%	5.74%	7.55%
Average (wt.%)	2.53%	1.78%	6.43%	15.95%	0.57%	1.34%	4.79%	8.08%

Table S2: ICP-MS result of spent graphite after primary acid leaching

Element	Li	Co	Ni	Mn	Fe	P	Al	Cu
Batch 1 (wt.%)	0.20%	0.07%	0.20%	0.16%	0.70%	0.85%	1.60%	0.75%
Batch 2 (wt.%)	0.23%	0.09%	0.09%	0.11%	0.27%	0.92%	5.51%	1.12%
Batch 3 (wt.%)	0.29%	0.07%	0.04%	0.07%	0.83%	1.07%	9.40%	2.46%
Average (wt.%)	0.24%	0.08%	0.11%	0.11%	0.60%	0.95%	5.51%	1.44%

Table S3. Chemical reactions in the primary acid leaching¹

Chemical Reaction	ΔG (kJ mol ⁻¹)	
$6LiNi_{0.33}Mn_{0.33}Co_{0.33} + 9H_2SO_4 + 6FeSO_4 \rightarrow 2NiSO_4 + 2NiSO_4 + 2NiSO_4 + 12H_2O + 3Fe_2(SO_4)_3$	-1509.9	Eq. S1
$2LiFePO_4 + 3H_2SO_4 \rightarrow 2FeSO_4 + Li_2SO_4 + 2H_3PO_4$	-67.4	Eq. S2
$6LiNi_{0.33}Mn_{0.33}Co_{0.33} + 9H_2SO_4 + 3H_2O_2 \rightarrow 2NiSO_4 + 2NiSO_4 + 2NiSO_4 + 12H_2O + 3O_2$	-1078.6	Eq. S3

Table S4. The standard hydrogen potentials of electrochemical reactions²

Electrochemical reaction	E_{eq} vs. SHE (30 °C)	
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.667	Eq. S4
$Cu^{2+} + 2e^- \rightarrow Cu$	0.337	Eq. S5
$2H^+ + 2e^- \rightarrow H_2$	0	Eq. S6
$Al^{3+} + 3e^- \rightarrow Al$	-1.681	Eq. S7

Table S5. ICP-MS result of recovered graphite via a one-step acid leaching

Element	Li	Co	Ni	Mn	Fe	P	Al	Cu
Batch 1 (wt.%)	0.29%	0.21%	0.71%	1.38%	0.10%	0.13%	0.42%	0.36%
Batch 2 (wt.%)	0.39%	1.71%	1.52%	0.51%	0.33%	0.05%	1.34%	0.22%
Batch 3 (wt.%)	0.35%	0.25%	0.84%	1.72%	0.10%	0.14%	0.32%	0.49%
Batch 4 (wt.%)	0.26%	0.60%	1.01%	0.37%	0.14%	0.05%	1.70%	0.13%

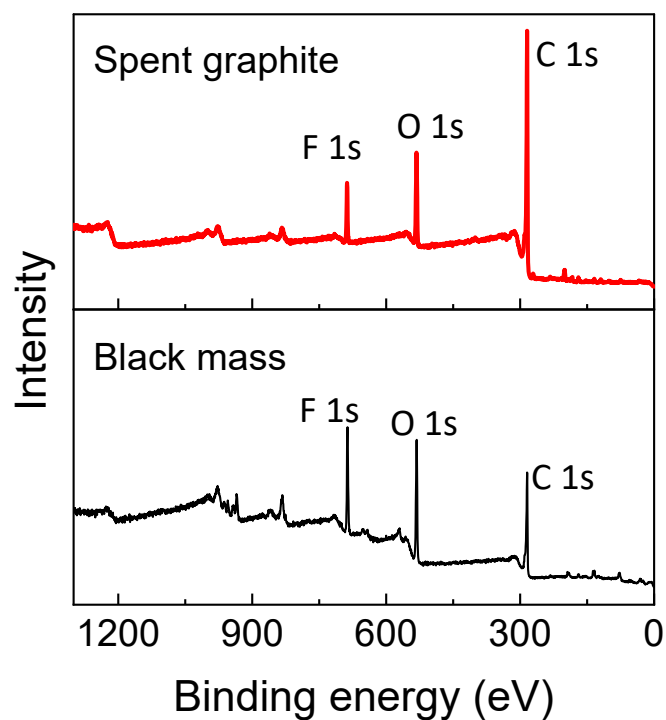


Figure S1. XPS spectra of black mass and spent graphite.

Spent graphite

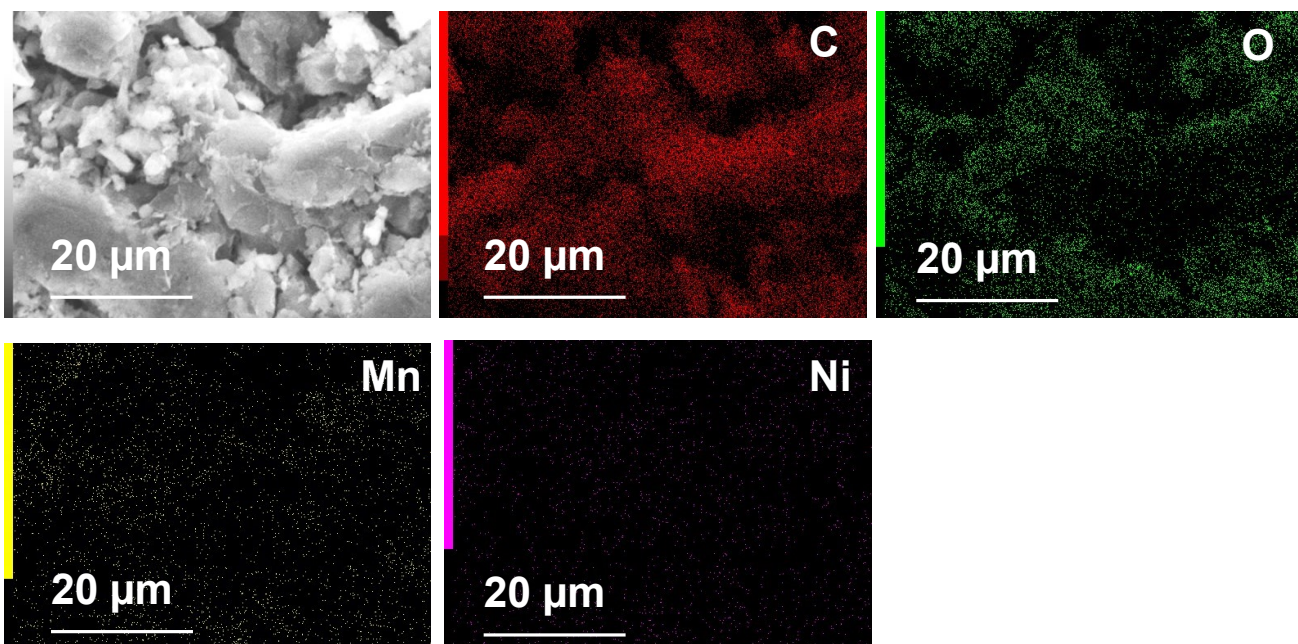
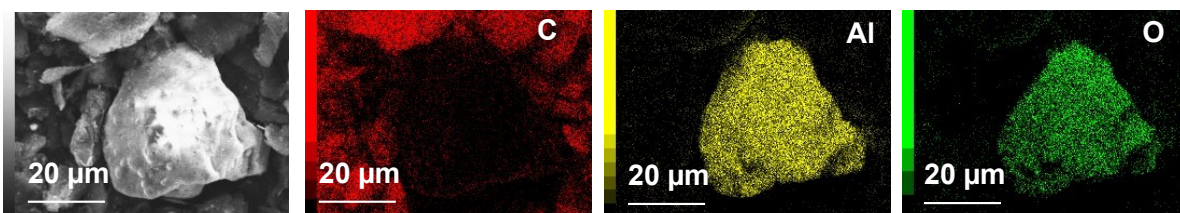
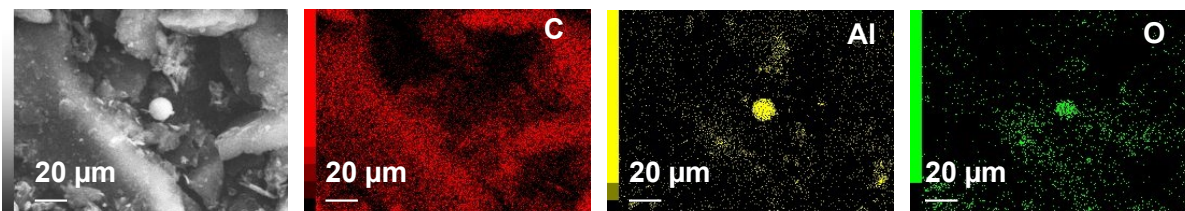


Figure S2. SEM-EDS mapping of spent graphite.

AG-1.0M



AG-1.5M



AG-2.0M

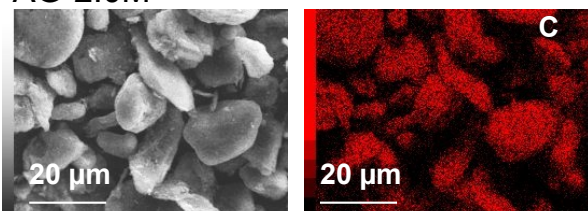


Figure S3. SEM-EDS mapping of AG- x M samples. AG- x M samples, where x represents H_2SO_4 concentration.

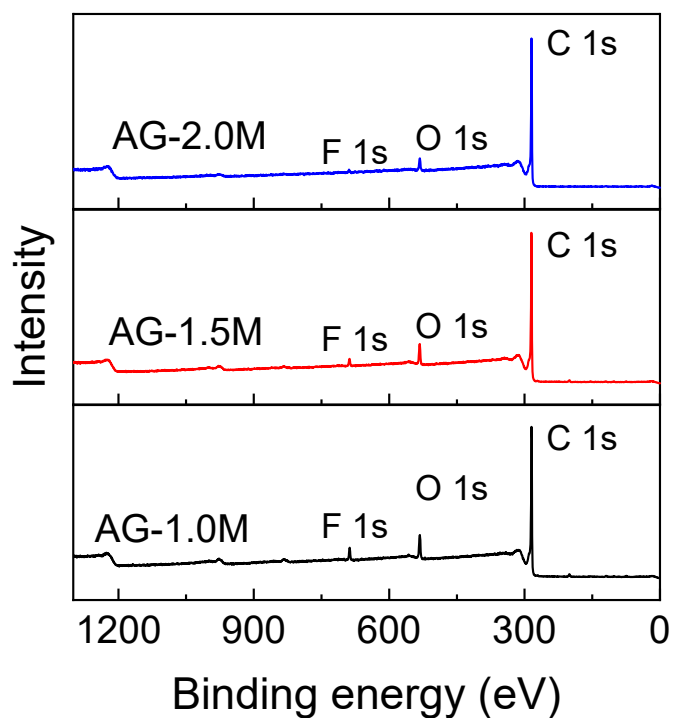


Figure S4. XPS spectra of acid-leached graphite samples. AG- x M samples, where x represents H_2SO_4 concentration.

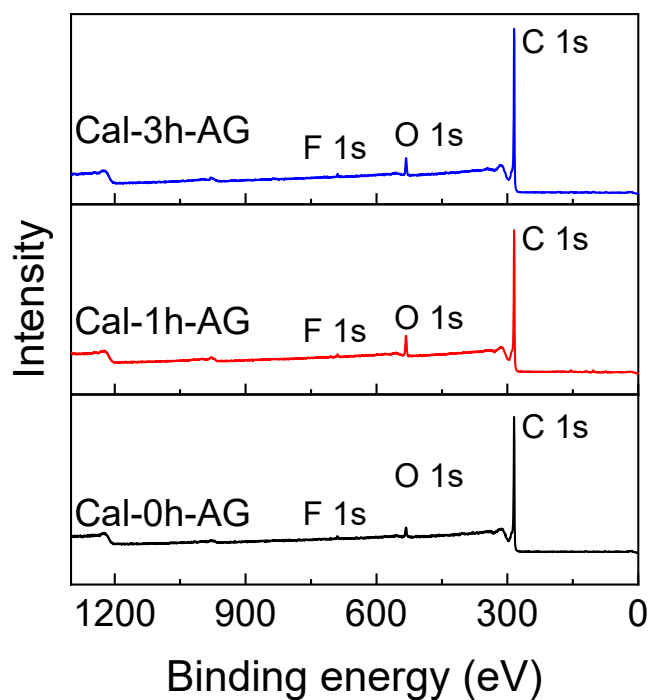


Figure S5. XPS spectra of graphite samples after calcination and acid leaching processes. Cal-*x*h-AG samples, where *x* represents calcination time. All the following acid leaching tests were used 1.5M H₂SO₄.

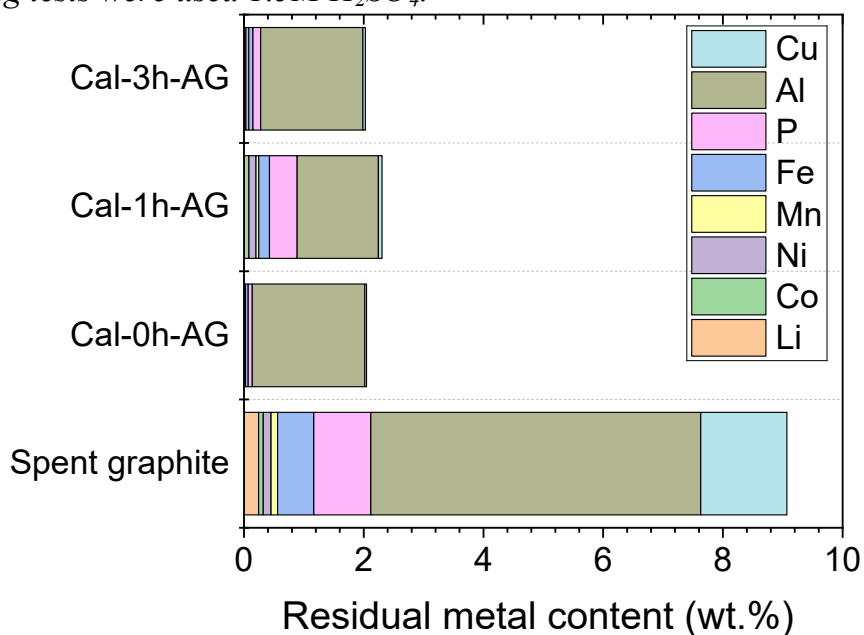


Figure S6. Residual metal content after calcination and leaching processes except F. Cal-*x*h-AG samples, where *x* represents calcination time. All the following acid leaching tests were used 1.5M H₂SO₄.

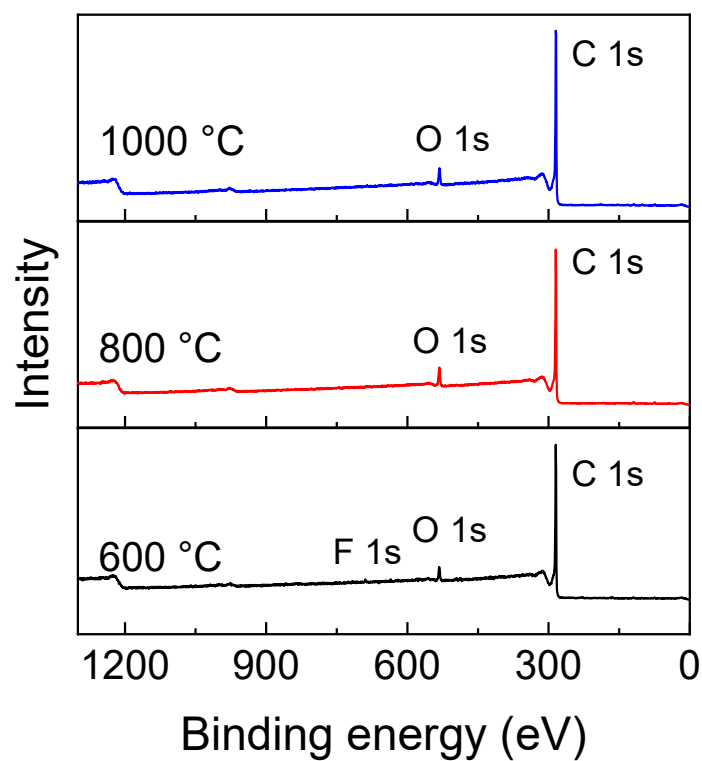


Figure S7. XPS spectra of spent graphite samples after sintered at 600 °C, 800 °C and 1000 °C under N_2 .

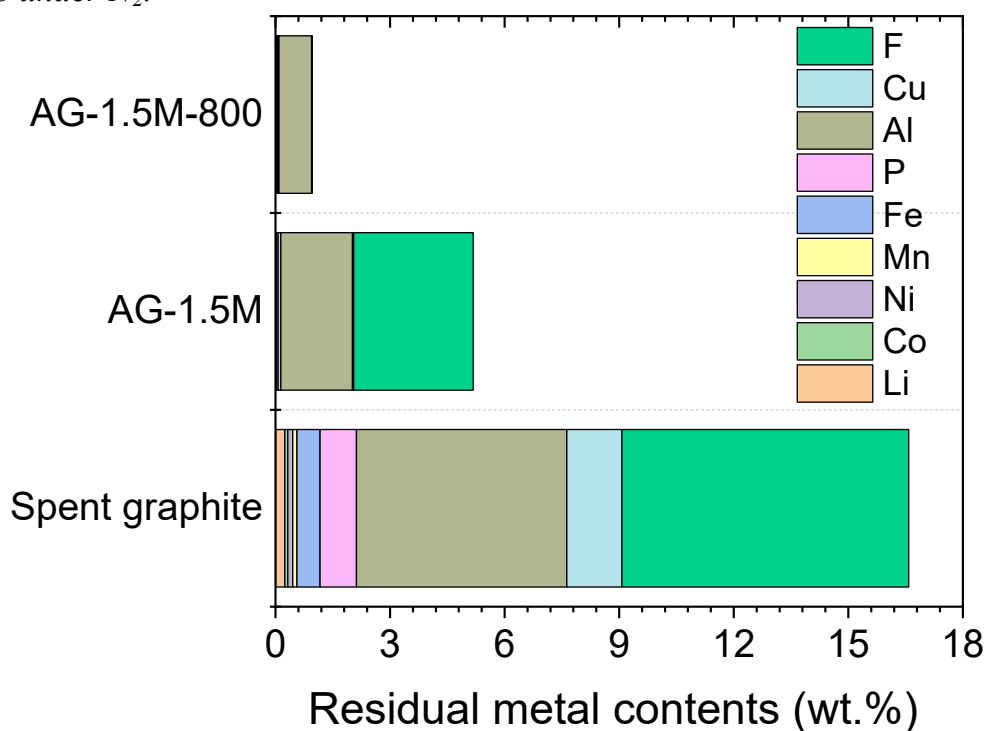


Figure S8. Residual metal contents using 1.5M H_2SO_4 as the acid concentration in the recycling process.

AG-2.0M-800

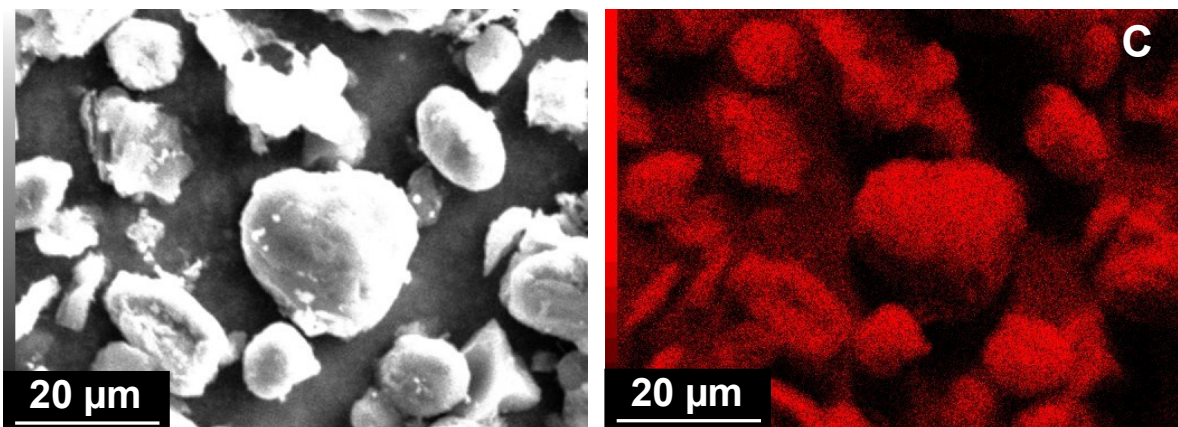


Figure S9. High-magnified SEM-EDS mapping of AG-2.0M-800 graphite sample.

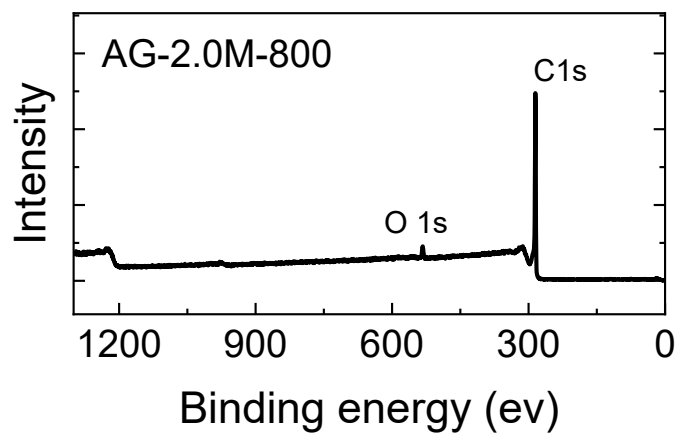


Figure S10. XPS spectra of AG-2.0M-800 graphite sample.

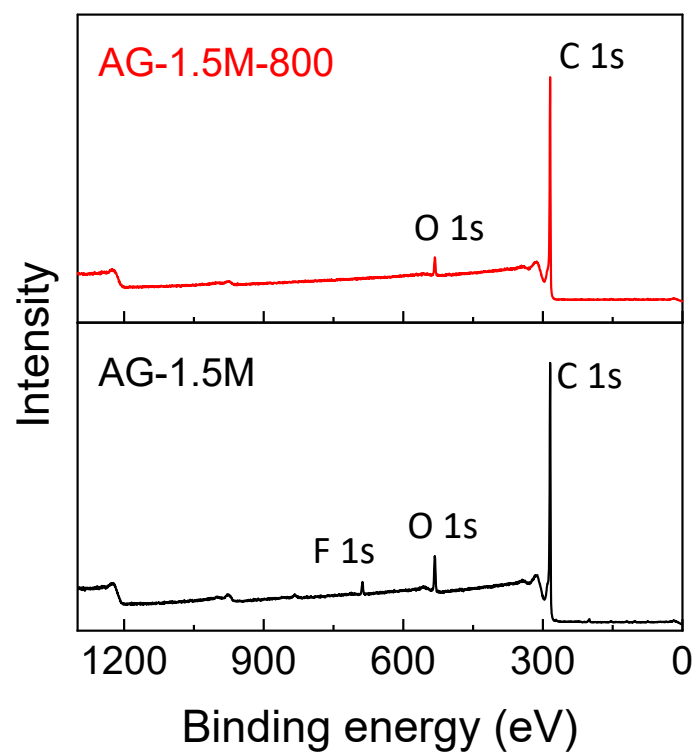


Figure S11. XPS spectra of AG-1.5M and AG-1.5M-800 graphite samples.

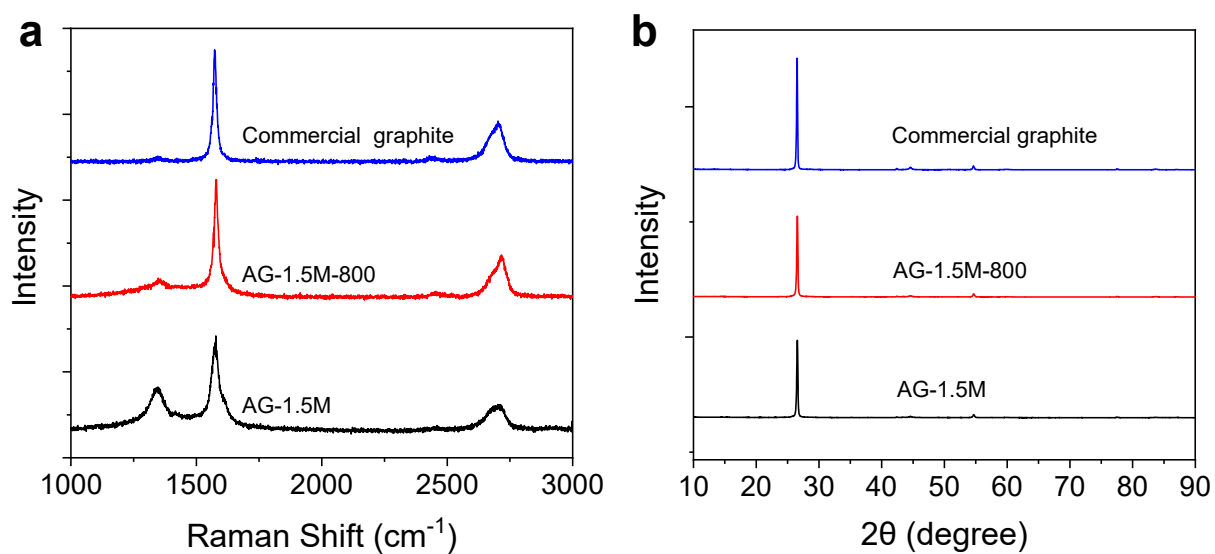


Figure S12. Characterization of commercial graphite, AG-1.5M and AG-1.5M-800 graphite samples. (a) Raman spectra. (b) XRD spectra.

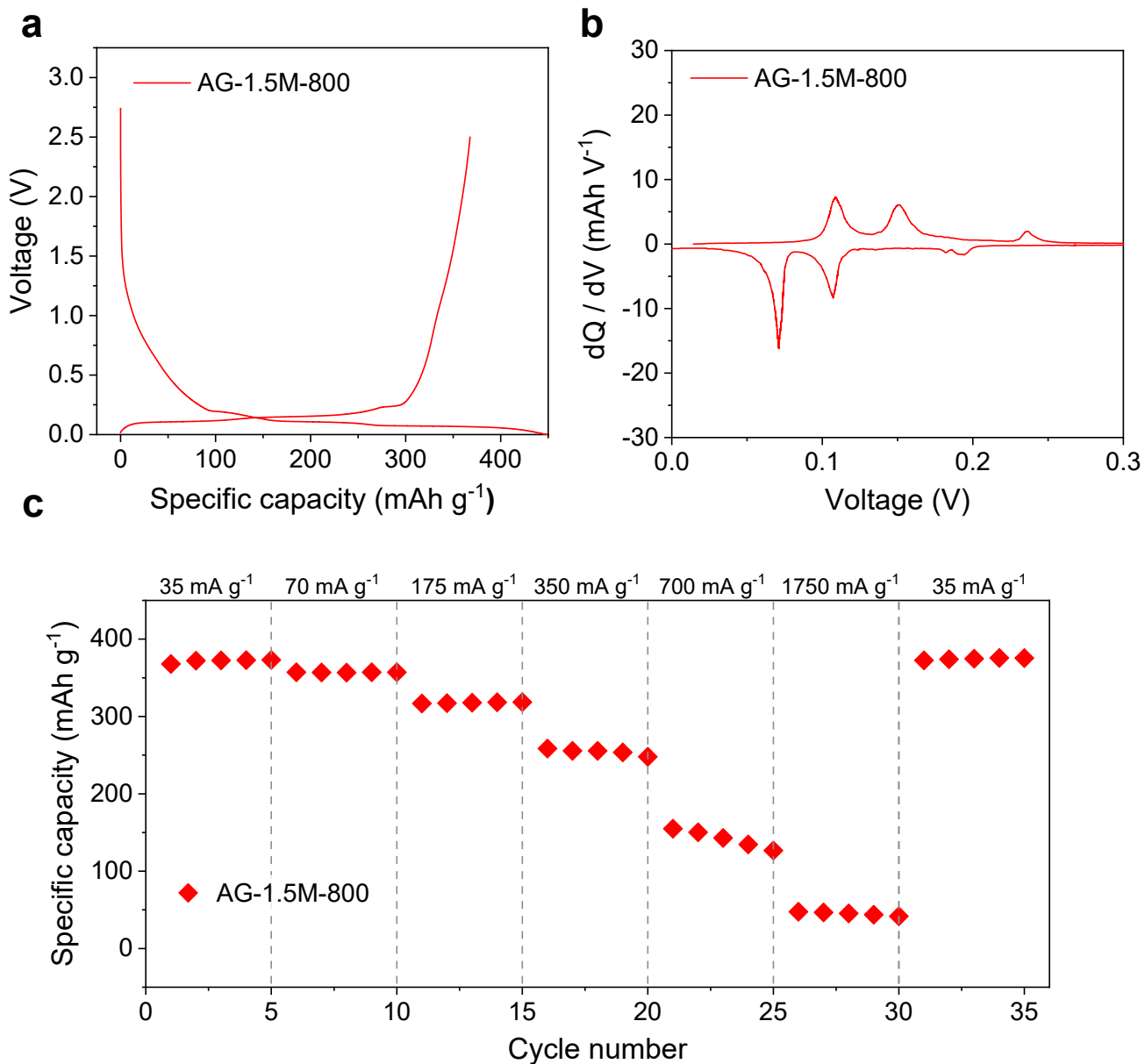


Figure S13. The electrochemical performance of AG-1.5M-800 graphite sample. (a) The first charge-discharge cycle voltage profile at 0.1C. (b) dQ vs dV profiles. (c) Rate performance.

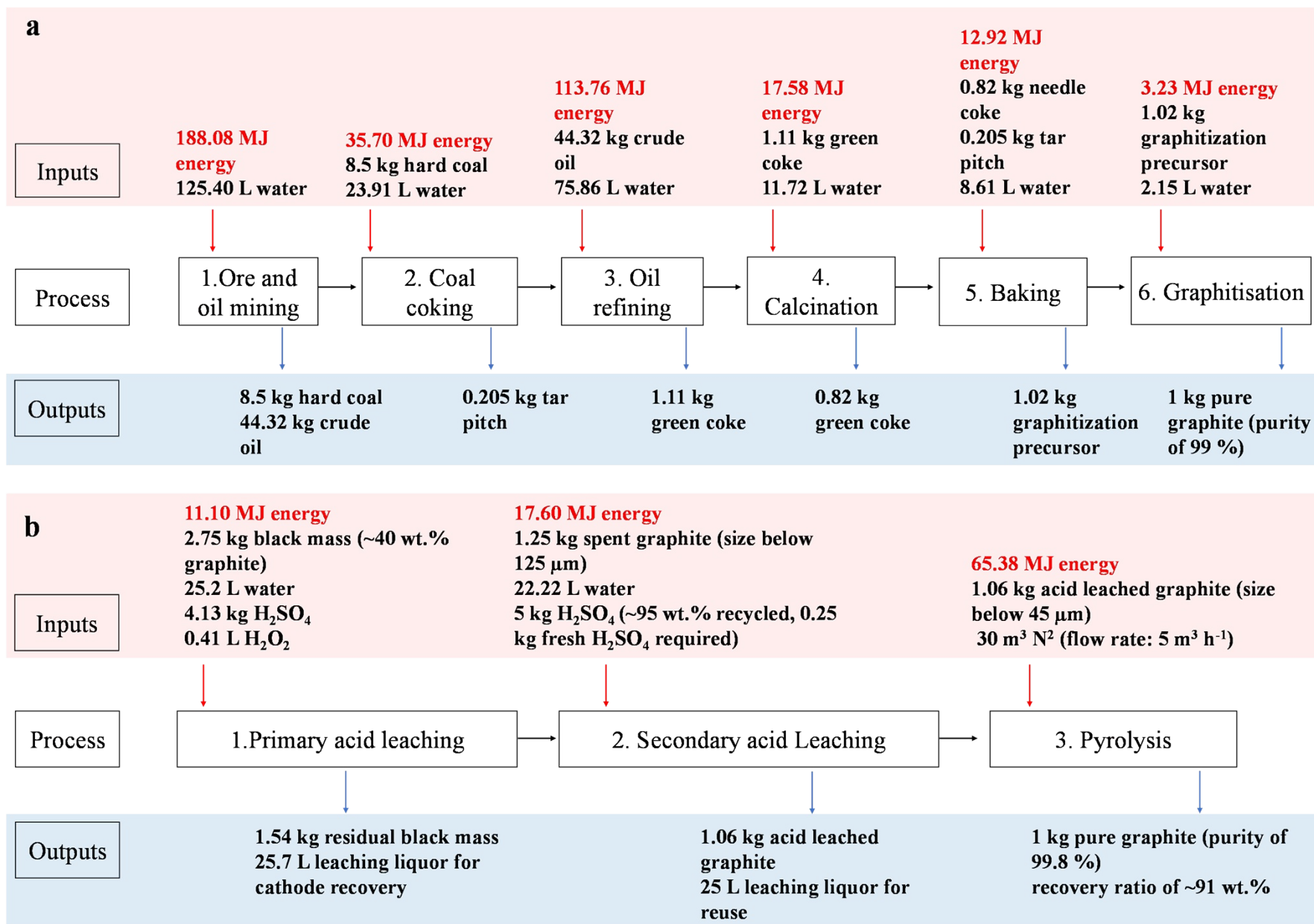


Figure S14. Process flow diagrams of various battery-grade graphite production routes, including inputs and outputs. a) Synthetic battery-grade graphite production.³ b) Proposed battery-grade graphite recycling in this work.

Energy consumption estimation

To determine the energy input necessary for conducting acid leaching while maintaining a constant temperature, two components must be considered: first, the energy required to heat the solution to the desired temperature; and second, the energy needed to compensate for heat loss over time.

$$Q_{total} = Q_{heat} + Q_{loss}$$

The energy required to heat the material from room temperature to the desired temperature can be calculated using the equation:

$$Q_{heat} = m \cdot c \cdot \Delta T$$

Where:

- Q_{heat} = heat energy required (J)
- m = mass of the solution (kg)
- c = specific heat capacity of the solution ($\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$)
- ΔT = change in temperature = $T_{final} - T_{initial}$ ($^\circ\text{C}$)

To maintain the solution at a constant temperature, it is necessary to continuously supply energy to compensate for heat losses to the surrounding environment. This requirement is influenced by several factors, including the quality of insulation, ambient temperature, and the characteristics of the solution. Heat loss can typically be estimated using the following equation:

$$Q_{loss} = \frac{U \cdot A \cdot (T_{final} - T_{ambient}) \cdot t}{\eta}$$

Where:

- Q_{loss} = heat energy lost over time (J)
- U = overall heat transfer coefficient ($\text{W m}^{-2} \text{ }^\circ\text{C}^{-1}$)
- A = surface area of the solution container exposed to the surroundings (m^2)
- $T_{ambient}$ = ambient temperature ($^\circ\text{C}$)
- t = time you want to maintain the temperature (s)
- η = efficiency of the heating system (0-1)

However, under these circumstances, the heat loss is simplified by expressing the heat loss rate as a percentage of the heater's power output, due to the absence of specific parameters.

$$Q_{loss} = \alpha \cdot Q_{equipment} = \alpha \cdot Pt$$

Where:

- α = a heat loss ratio (0-1)
- P = the power of the heating system (W)
- t = overall heating time (s)

Table S6. Parameters for energy consumption

Parameter	Symbol	Value	Unit
Reaction Temperature in acid leaching	T	90	°C
Room Temperature	T	25	°C
Specific heat capacity of the solution in primary acid leaching	c	4186	J kg ⁻¹ °C ⁻¹
Specific heat capacity of graphite	c	710	J kg ⁻¹ °C ⁻¹
The power of heating in acid leaching	P	1500	W
The power of pyrolysis furnace	P	10000	W
Primary acid leaching time	t	0.67	h
Secondary acid leaching time	t	3	h
Pyrolysis time	t	6	h
Heat efficiency in acid leaching	α	0.1	
Heat efficiency in pyrolysis	α	0.3	

Reference

1. Zou, Y., Chernyaev, A., Ossama, M., Seisko, S. & Lundström, M. Leaching of NMC industrial black mass in the presence of LFP. *Scientific Reports* 2024 14:1 14, 1–14 (2024).
2. Chernyaev, A. *et al.* The efficiency of scrap Cu and Al current collector materials as reductants in LIB waste leaching. *Hydrometallurgy* 203, 105608 (2021).

3. Chen, W. *et al.* Flash Recycling of Graphite Anodes. *Advanced Materials* 35, 2207303 (2023).