

1 Analysis of Pretreatment

Fig. S1 presents the TG-DSC curves of the untreated spent LIBs BM, recorded at a heating rate of 5 °C/min under a mixed atmosphere (80 mL/min O₂ and 320 mL/min N₂) using a thermal analyzer (STA300, Hitachi High-Tech Corporation, Tokyo, Japan). The thermal analysis reveals three distinct weight loss stages from 28 °C to 700 °C. Specifically, the initial endothermic event (Peak A at 203 °C) and the minor mass loss below 370 °C are attributed to the volatilization of moisture and residual electrolytes. The subsequent progressive weight loss up to 550 °C corresponds to the continuous decomposition of organic binders, such as polyvinylidene fluoride (PVDF). Beyond 550 °C, the DSC curve rises sharply to a prominent exothermic peak (Peak B) at 596 °C, accompanied by a substantial mass loss of 30.62%. This indicates the vigorous oxidative combustion of graphite, potentially accompanied by carbothermic reduction reactions.

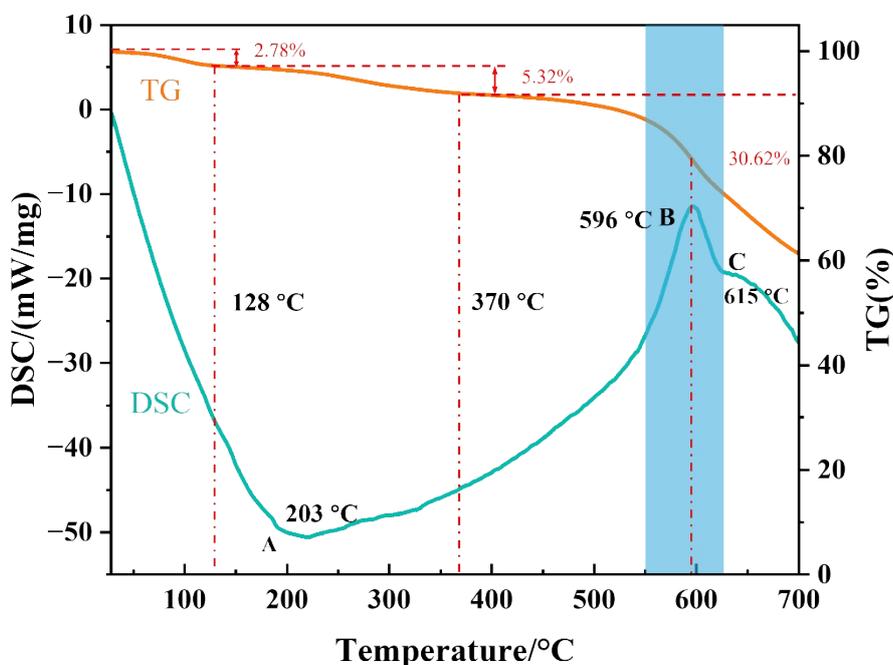


Fig. S1 TG-DSC curves of spent LIBs BM

2 Economic analysis and environmental implications

2.1 Economic comparison of alternative schemes

Table S1 A brief review of published laboratory work on Pyro-hydrometallurgy recycling process.

NO.	Cathode materials	Optimized conditions	Recovery efficiency	Ref.
1	LIBs black mass	<ul style="list-style-type: none"> • Fe₂O₃; Mass ratio = 1.6:2 • 650°C for 90 min • Water leaching 80°C 2h 50g/L 	89.65% Li, 62.35% Ni, 89.18% Co, 96.75% Mn, 91.05% Cu	This work

2	LCO	<ul style="list-style-type: none"> • MnSO_4; $n_{(\text{MnSO}_4)}/n_{(\text{LiCoO}_2)}=1:2$ • 700 °C for 30 min • Water leaching 40°C, 2.5mL/g 	99.35% Li	1
3	NCM	<ul style="list-style-type: none"> • H_2SO_4; $n_{(\text{H}_2\text{SO}_4)}/n_{(\text{Li})}=\mathbf{0.95:1}$ • 550 °C for 180 min • Water leaching 30°C, 4 mL/g, 2h • Acid leaching 2 mol/L, 60°C, 5 mL/g, 2h 	90% Li, 98% Ni, 97% Co, 90% Mn	2
4	NCM	<ul style="list-style-type: none"> • $(\text{NH}_4)_2\text{SO}_4$; $n_{[(\text{NH}_4)_2\text{SO}_4]}/n_{[\text{2Li}]} = 1.1)$ • 650 °C for 300 min • Water leaching 	90.3% Li	3
5	LCO	<ul style="list-style-type: none"> • $\text{K}_2\text{S}_2\text{O}_7$; $m_{(\text{K}_2\text{S}_2\text{O}_7)}/m_{(\text{LCO})}= 2:3$ • 800 °C for 120 min • Water leaching 25°C, 100min, 20g/L 	98.51% Li	4
6	LCO	<ul style="list-style-type: none"> • FeS_2 $m_{(\text{FeS}_2)}/m_{(\text{LCO})}= 2:1$ • 800 °C for 60 min • Water leaching 25°C, 30min, 50g/L 	99.97% Li, 0.08% Co	5
7	NCM	<ul style="list-style-type: none"> • 19.9 wt% carbon dosage • 650 °C for 180 min • 3.5 M H_2SO_4 at 85 °C for 3 h, 200g/L 	84.7% Li, more than 99% Co, Ni and Mn	6

To streamline the computation, we make the assumption that the leaching apparatus is heated using a thermostat water bath with a 500 W heating power and a heating speed of 3 °C/min. The roasting equipment is heated by a muffle furnace with a heating speed of 5 °C /min and a heating power of 3 kW (room temperature: 25 °C). The average industrial power rate in China is approximately US\$0.084/kWh.

Table S2 Costs of the recycling process when recycling 1kg materials.

NO.	Optimized conditions	Acid cost	Reductant cost	Heating cost	Total cost	Ref.
1	<ul style="list-style-type: none"> ● Fe₂O₃; Mass ratio = 1.6:2 ● 650°C for 90 min ● Water leaching 80°C 2h 	-	-	\$1.00	\$1.00	This work
2	<ul style="list-style-type: none"> ● MnSO₄; n_{(MnSO₄)/n_(LiCoO₂)=1:2} ● 700 °C for 30 min ● Water leaching 40°C 	-	\$0.46	\$0.74	\$1.20	1
3	<ul style="list-style-type: none"> ● H₂SO₄; n_{(H₂SO₄)/n_(Li)=0.95:1} ● 550 °C for 180 min ● Acid leaching 2 mol/L, 60°C, 5 mL/g, 2h 	\$0.10	-	\$1.37	\$1.47	2
4	<ul style="list-style-type: none"> ● (NH₄)₂SO₄; n_(NH₄)₂SO₄)/n_[2Li] = 1.1) ● 650 °C for 300 min ● Water leaching 	-	\$0.45	\$1.79	\$2.24	3
5	<ul style="list-style-type: none"> ● K₂S₂O₇; m_{(K₂S₂O₇)/m_(LCO)= 2:3} ● 800 °C for 120 min ● Water leaching 25°C, 100min, 20g/L 	-	\$0.80	\$1.16	\$1.96	4
6	<ul style="list-style-type: none"> ● FeS₂ m_{(FeS₂)/m_(LCO)= 2:1} ● 800 °C for 60 min ● Water leaching 25°C, 30min, 50g/L 	-	\$0.16	\$0.90	\$1.06	5
7	<ul style="list-style-type: none"> ● 19.9 wt% carbon dosage ● 650 °C for 180 min ● 3.5 M H₂SO₄ at 85 °C for 3 h, 200g/L 	\$0.17	\$0.10	\$1.42	\$1.69	6

2.2 Economic comparison of alternative schemes

2.2.1 Material analysis

The economic analyses in this study are based on an example of 1000 kg of lithium battery black powder, which was economically evaluated for laboratory-scale lithium battery black powder recycling based on the proposed process. Details are given below:

For processing 1000 kg of spent LIBs BM, the optimum roasting conditions were determined as follows: the mass ratio of Fe₂O₃ to spent LIBs BM (after heat treated) = 1.6:2, the roasting temperature: 650 °C, the roasting time: 90 min, atmosphere: 20ml/minSO₂-80ml/min O₂-300ml/min Ar. And the recoveries of the valuable metals under these conditions were 89.65% Li, 62.35% Ni, 89.18% Co, 96.75% Mn, and 91.05% Cu, of which 98.87% Fe₂O₃ was retained in the residue. Therefore, 32.18kg Li, 5.18kg Ni, 268.07kg Co, 11.51kg Mn, 5.37kg Cu can be recovered.

2.2.2 Energy analysis

(1) Removal of organic binder: The spent LIBs BM was heated to 550 °C to remove the organic binder.

According to the pretreatment procedure, the electrical energy required for 4 hours of roasting at 550 °C is calculated as $4 \text{ h} \times 30 \text{ kW} = 120 \text{ kWh}$.

(2) Roasting of spent LIBs BM with Fe_2O_3 : According to the optimal roasting conditions in the article to determine the roasting temperature of 650 °C, the roasting time of 90 min, under these conditions the furnace roasting power required for $1.5 \times 30 \text{ kW} = 45 \text{ kWh}$

(3) Water leaching of the calcine: The thermal energy required for the leaching process is provided by the waste heat of the hot gas released during the roasting process.

2.2.3 Estimated electrical energy requirements for selected units of the process

(1) Calculation of electric power for motor-driven rotary kiln: The required power is calculated by the following simplified formula:

$$N = K \times \log(D) \times Q$$

where N is the power required by the rotary kiln (kW), D is the internal diameter of the kiln (m), Q is the daily clinker production (t/d), and K is a coefficient related to the shape of the rotary kiln (assuming $K = 1.3$).

Assuming that 1000,000 tons of lithium cobalt batteries are processed, the daily output of the rotary kiln is 3333.33 tons ($1000,000 \div 300$). The power required by the rotary kiln (kiln diameter $D = 6$ meters, kiln length $L = 90$ meters) is

$$N = 1.3 \times \log(6) \times 3333.3 = 3370 \text{ (kW)}$$

Therefore, the electrical energy consumption of the roasting unit is approximately $(3370 \times 24)/3333 = 24$ kWh/ton of LIBs BM.

(2) Heat loss of rotary kiln: the heat loss of rotary kiln is mainly the heat exchange between the outer wall of the kiln and the environment, and the heat loss is divided into two parts: convective heat transfer loss and radiative heat transfer loss. Heat loss can be calculated by equation.

$$Q = (h_c + h_r) A_w (t_w - t) = h_T A_w (t_w - t)$$

Where, Q is the total heat loss (kW), h_c , h_r and h_T indicate convective heat transfer coefficient, radiation heat transfer coefficient and joint heat transfer coefficient ($\text{W}/\text{m}^2 \cdot \text{K}$), A_w is the wall area (m^2), t_w and t are the wall temperature and air temperature (°C). In the calculation of the joint heat transfer coefficient, for the pipe, cylinder wall using the empirical formula.

$$h_T = 9.4 + 0.052(t_w - t)$$

The average temperature on the surface of the rotary kiln is about 150 °C. Assuming an ambient site

temperature of 25 °C, the joint heat feeding coefficient $h_T = 15.9 \text{ W/m}^2\cdot\text{K}$ can be calculated and the heat loss of the rotary kiln is 140 kW h^{-1} .

Table S3. Value of recycled materials (\$/kg).

	Li⁺ in product	Ni²⁺ in product	Co²⁺ in product	Mn²⁺ in product	Cu²⁺ in product	Fe₂O₃
\$/kg	70	13	52	3	9	0.3

2.2.4 Economic assessment of the whole process

(1) The recycling of 1000 kg of spent LIBs BM through sulfidation roasting and water leaching yields the following recoveries of valuable metals: Li⁺ at \$2252.60, Ni²⁺ at \$67.34, Co²⁺ at \$13,939.64, Mn²⁺ at \$34.53, and Cu²⁺ at \$48.33. The cost of the LIBs BM is \$7.39/kg, totaling \$7390 for 1000 kg.

(2) Electricity cost: The total net demand of electric energy is 329 kWh. Assuming that the heat is provided by electric energy during the experiment, the average industrial electricity price in China is about \$0.084/kWh. Therefore, the total cost of electrical energy consumption is about \$30.

(3) The total profit of the whole process: After roasting 2300 kg of metallurgical residue (as the Fe₂O₃ catalyst source) (as the Fe₂O₃ catalyst source, nickel slag, for example - about 50% iron, optimal mass ratio conditions) to leach 1000 kg of lithium battery black powder, the revenue of recovered products is about 16342.44 \$, and finally about 1581.9 kg of iron oxide (0.3 \$/kg) can be recovered, with a revenue of 474.68 \$, after deducting the cost of electricity and the initial input cost, the total profit is 16342.44 \$. After deducting the cost of electricity and the initial input cost, the total profit is $16342.44 + 474.6 - 7390 - 30 = 9397$ \$/t(BM).

2.3 Economic Comparison of Traditional Processes

Assessing the financial viability of emerging recycling technologies is a crucial prerequisite for their industrial implementation. To this end, a systematic techno-economic assessment (TEA) was conducted to benchmark the proposed green sulfidation roasting process against conventional pyrometallurgical and hydrometallurgical routes. The processing of 1 kg of spent LIBs BM was defined as the functional unit for this evaluation. The inventory of fundamental material and energy consumption is detailed in Table S4^{7, 8}. The core economic advantage of the proposed process stems from its "synergistic waste valorization" strategy. Conventional recycling pathways are typically hindered by substantial cost constraints: pyrometallurgy is heavily penalized by the high energy consumption of high-temperature operations, whereas hydrometallurgy relies heavily on vast quantities of expensive chemical lixiviants. In contrast, this approach innovatively integrates SO₂-rich industrial flue gas into the reaction system to serve

simultaneously as both a reductant and a sulfidation agent. This entirely circumvents the need for conventional reducing agents such as coke. Process calculations indicate that treating 1 kg of LIBs BM synergistically consumes approximately 5.98 kg of waste SO₂ gas.

Based on the comprehensive treatment costs of existing flue gas desulfurization (FGD) systems^{9, 10}, (0.60-1.40 \$·kg⁻¹ SO₂), and taking the median value of 1.00 \$·kg⁻¹, the pollutant absorption achieved by this process translates into an environmental ‘avoided cost’ benefit of approximately 5.98 \$·kg⁻¹. As detailed in Table S5, the summation of this environmental benefit with the metal recovery value yields a total process revenue of 22.56 \$·kg⁻¹.

Table S4. Materials and energy requirements to recycle 1 kg of LIBs BM through different recycling technologies

		Pyrometallurgy	Hydrometallurgy	Sulfidation roasting with Fe ₂ O ₃
Materials requirements (kg)	Hydrochloric Acid	0.23	0.01	-
	Hydrogen Peroxide	0.07	0.41	-
	Limestone	0.32	-	0.05
	Sand (Silica flux)	0.17	-	-
	Sulfuric Acid	-	1.20	-
Energy requirements (MJ)	coke	0.08	-	-
	Natural gas	1.12	1.12	-
	Electricity	1.37	0.14	1.18

Table S5. Revenue of material recovered from different recycling processes.

	Value of recycled materials (\$·kg ⁻¹)	Sulfidation roasting with Fe ₂ O ₃ (\$·kg ⁻¹ , LIBs BM)	Pyrometallurgy (\$·kg ⁻¹ , LIBs BM)	Hydrometallurgy (\$·kg ⁻¹ , LIBs BM)
Co ²⁺ in product	52.00	13.94	14.07	14.85
Ni ²⁺ in product	13.00	0.07	0.10	0.10
Cu ²⁺ in product	9.00	0.05	0.05	0.05
Li ⁺ in product	70.00	2.25	-	2.01
Mn ²⁺ in product	3.00	0.03	-	0.03
Fe ₂ O ₃	0.30	0.24	-	-
Removal of sulfur dioxide from industrial flue gas	1.00	5.98	-	-
Total		22.56	14.22	17.04

In terms of cost-effectiveness, the proposed roasting strategy exhibits equally remarkable advantages (Table S6). The utilization of inexpensive solid additives drastically reduces direct material expenditures. Furthermore, the phase transformation induced during roasting substantially enhances both metal conversion and separation selectivity. This simplifies subsequent hydrometallurgical separation and purification stages, thereby effectively curtailing indirect overheads, including wastewater treatment and associated energy consumption. Consequently, the total operational cost of the system is strictly constrained to 3.11 \$·kg⁻¹.

The comprehensive analysis of revenues and costs indicates that the anticipated net profit margin for this process could reach 19.45 \$·kg⁻¹ of LIBs BM. This represents an increase of 8.41 \$·kg⁻¹ over the traditional pyrometallurgical route and 5.91 \$·kg⁻¹ over the hydrometallurgical route, fully demonstrating its significant advantages in terms of both economic viability and environmental synergistic benefits.

Table S6. Costs and profits of different recycling processes. (\$·kg⁻¹, Spent LIBs BM)

	Pyrometallurgy	Hydrometallurgy	Sulfidation roasting with Fe ₂ O ₃
Revenue	14.22	17.28	22.56
		Direct Costs	
Utilities	0.05	0.02	0.03
Labor	0.50	0.60	0.60
Materials	0.13	0.39	0.10
Other direct cost	0.30	0.80	0.60
Total Direct Cost	0.98	1.81	1.33
		Fixed Costs	
Depreciation	1.20	0.80	0.80
Other fixed cost	0.40	0.33	0.28
Total Fixed Cost	1.60	1.13	1.08
		Overheads	
Plant overhead	0.40	0.50	0.40
General expenses	0.20	0.30	0.30
Total Cost	3.18	3.74	3.11
Profits	11.04	13.54	19.45

Reference

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