Supporting Information

Green strategy for recycling cathode materials from spent lithium-ion batteries using glutathione

Kunhong Gu[1], Xingyuan Gu[2], Yongwei Wang[1],Wenqing Qin[1], Junwei Han[1]*

1. *School of Minerals Processing & Bioengineering, Central South University, Changsha 410083, China*

2. *School of Traditional Chinese Medicine, Beijing University of Chinese Medicine, Beijing 100029, China*

Corresponding author: Junwei Han, hanjunwei@csu.edu.cn

The following are included in the supplementary information below:

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- **Fig. S3** Flow chart of the recycling process
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- **Fig. S5** Response surface diagram of the influence of H_2SO_4 concentration and leaching temperature on metal leaching efficiencies: (a)Li, (b)Ni, (c)Co, (d)Mn.
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- **Fig. S11** Fitting results of surface chemical reaction control model for metal leaching efficiencies in H_2SO_4+H_2O_2 leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn
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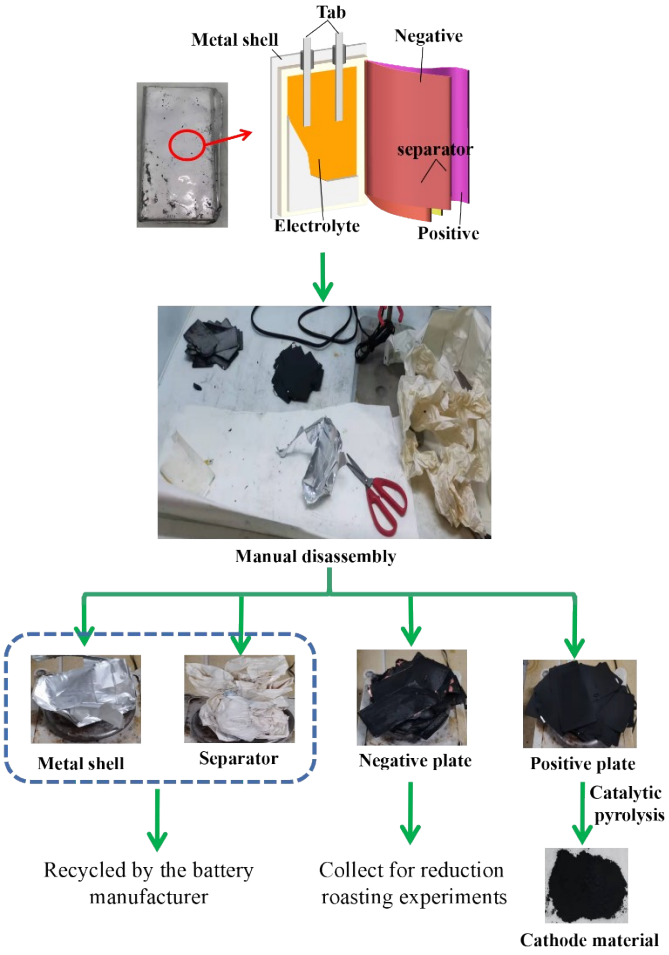

Fig. S1 The preparation process for raw materials

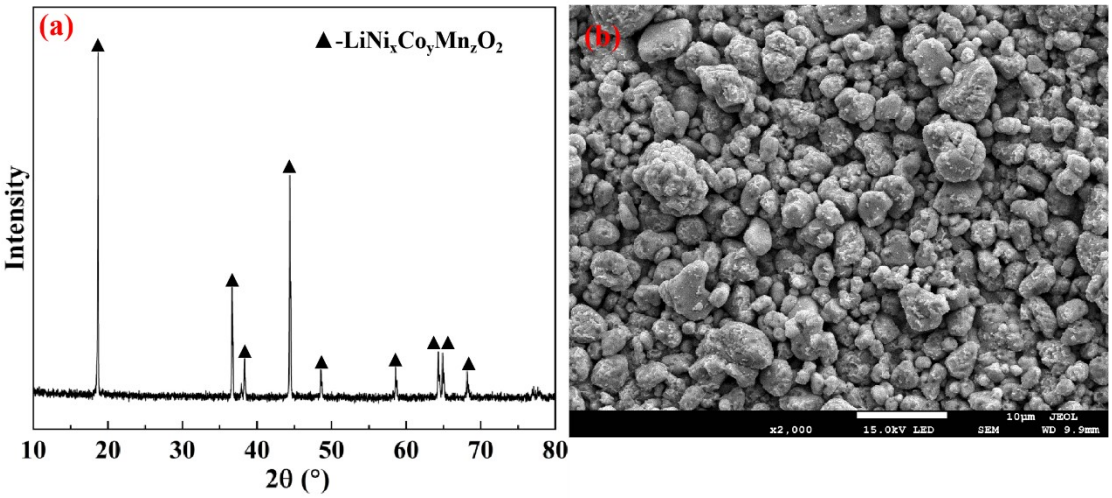

Fig. S2 XRD and SEM diagrams of raw materials.

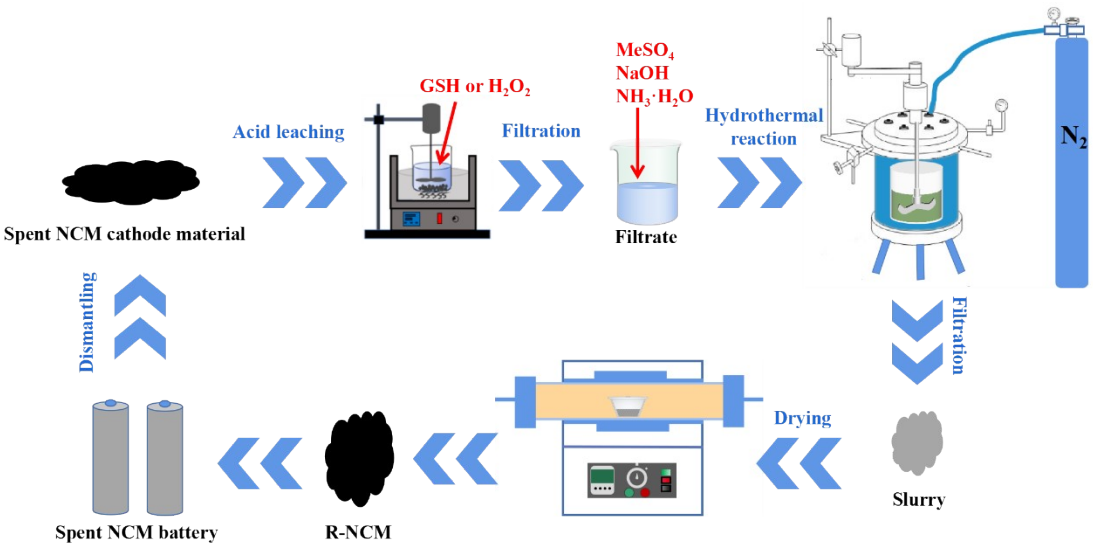

Fig. S3 Flow chart of the recycling process

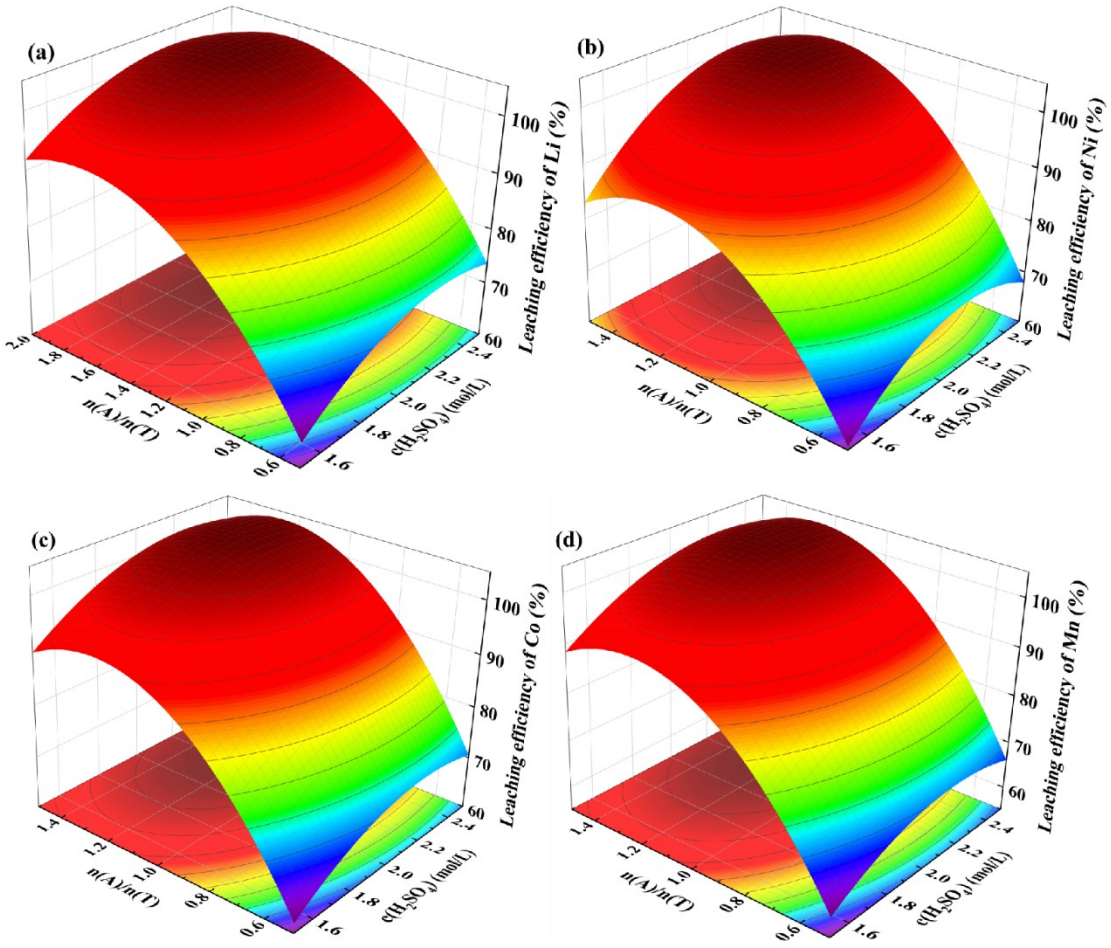

Fig. S4 Response surface diagram of the influence of H_2SO_4 concentration and GSH dosage(n(A)/n(T)) on metal leaching efficiencies: (a)Li, (b)Ni, (c)Co, (d)Mn.

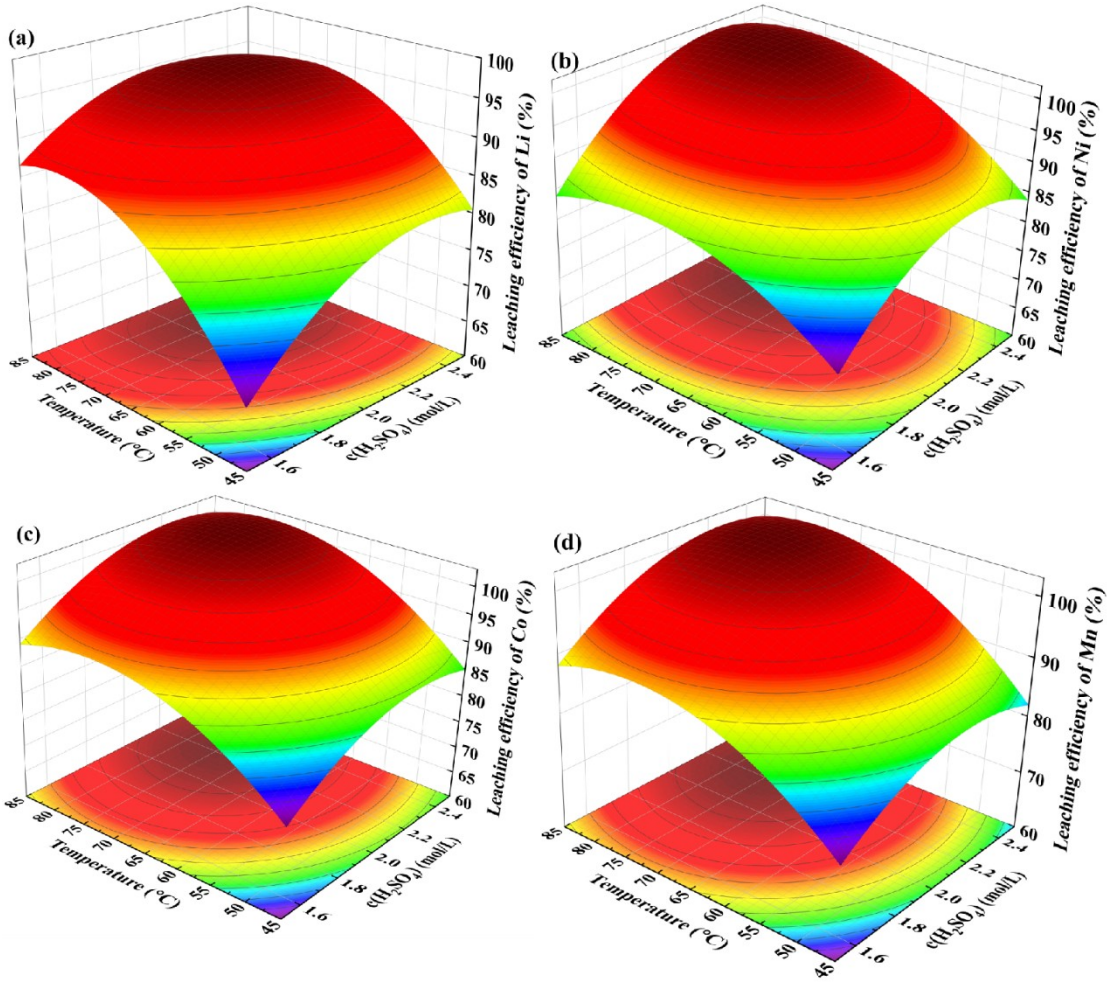

Fig. S5 Response surface diagram of the influence of H_2SO_4 concentration and leaching temperature on metal leaching efficiencies: (a)Li, (b)Ni, (c)Co, (d)Mn.

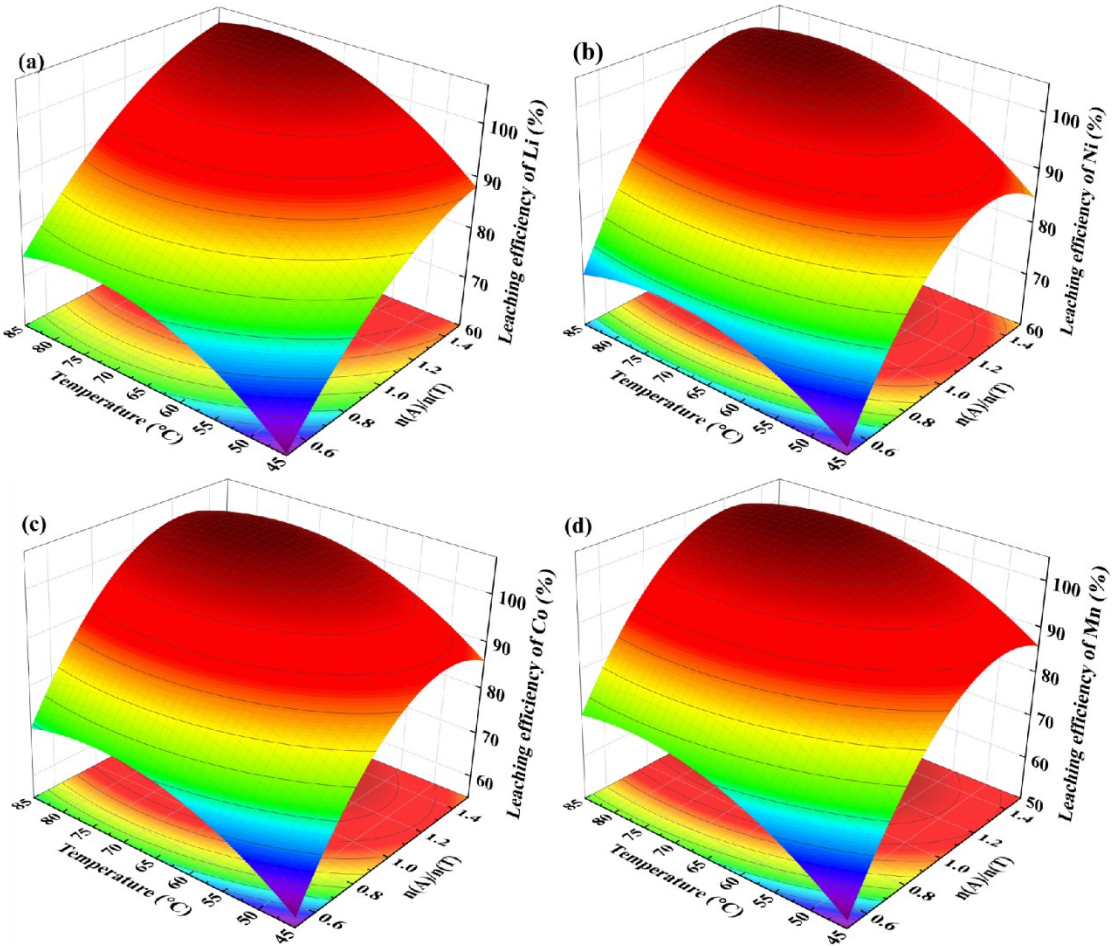

Fig. S6 Response surface diagram of the influence of GSH dosage(n(A)/n(T)) and leaching temperature on metal leaching efficiencies: (a)Li, (b)Ni, (c)Co, (d)Mn.

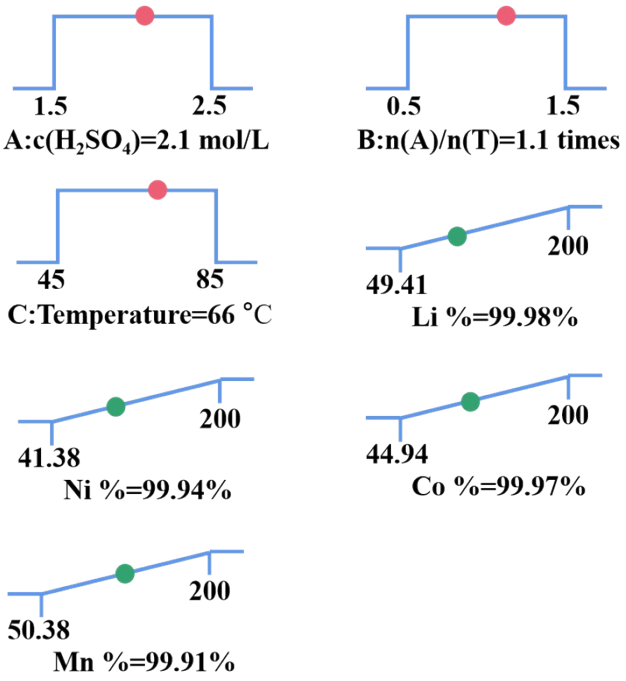

Fig. S7 Optimal leaching conditions and prediction of leaching efficiencies

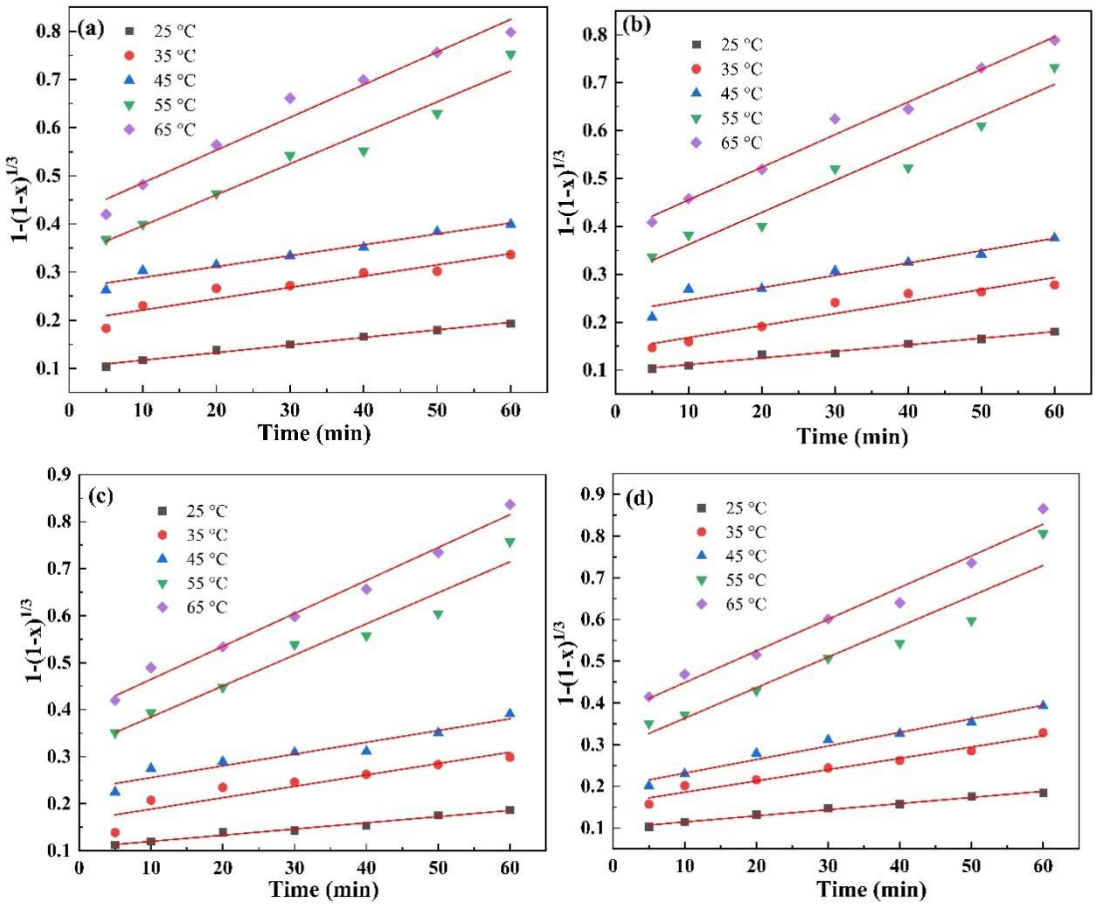

Fig. S8 Fitting results of surface chemical reaction control model for metal leaching efficiencies in H_2SO_4+GSH leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

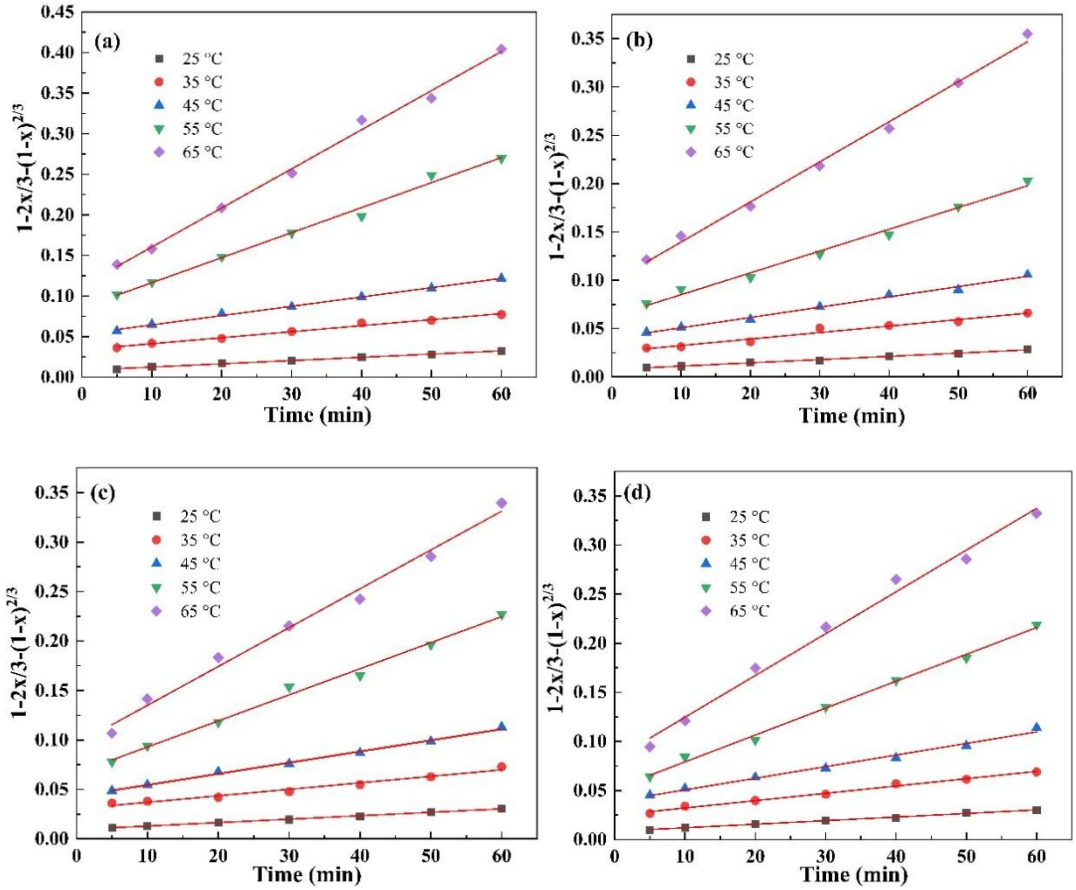

Fig. S9 Fitting results of internal diffusion control model for metal leaching efficiencies in H_2SO_4+GSH leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

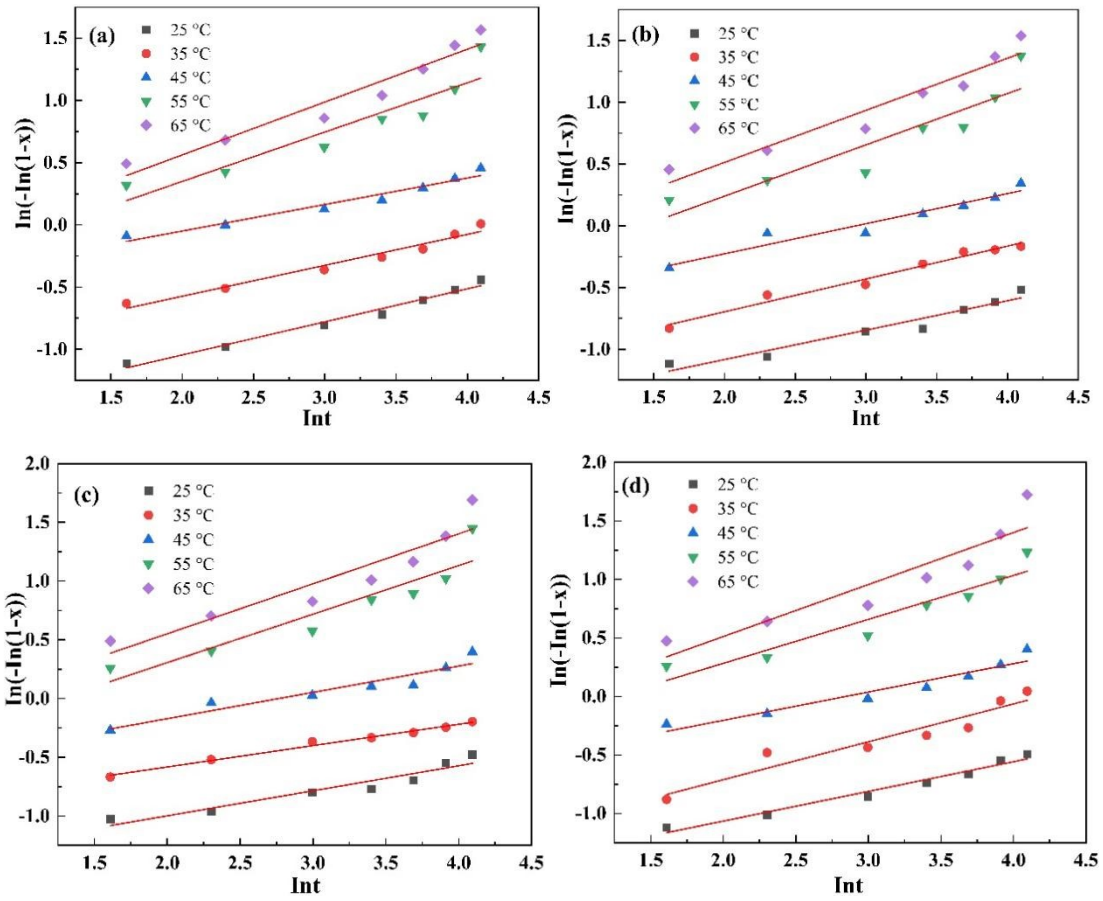

Fig. S10 Fitting results of Avrami equation for metal leaching efficiencies in H_2SO_4+GSH leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

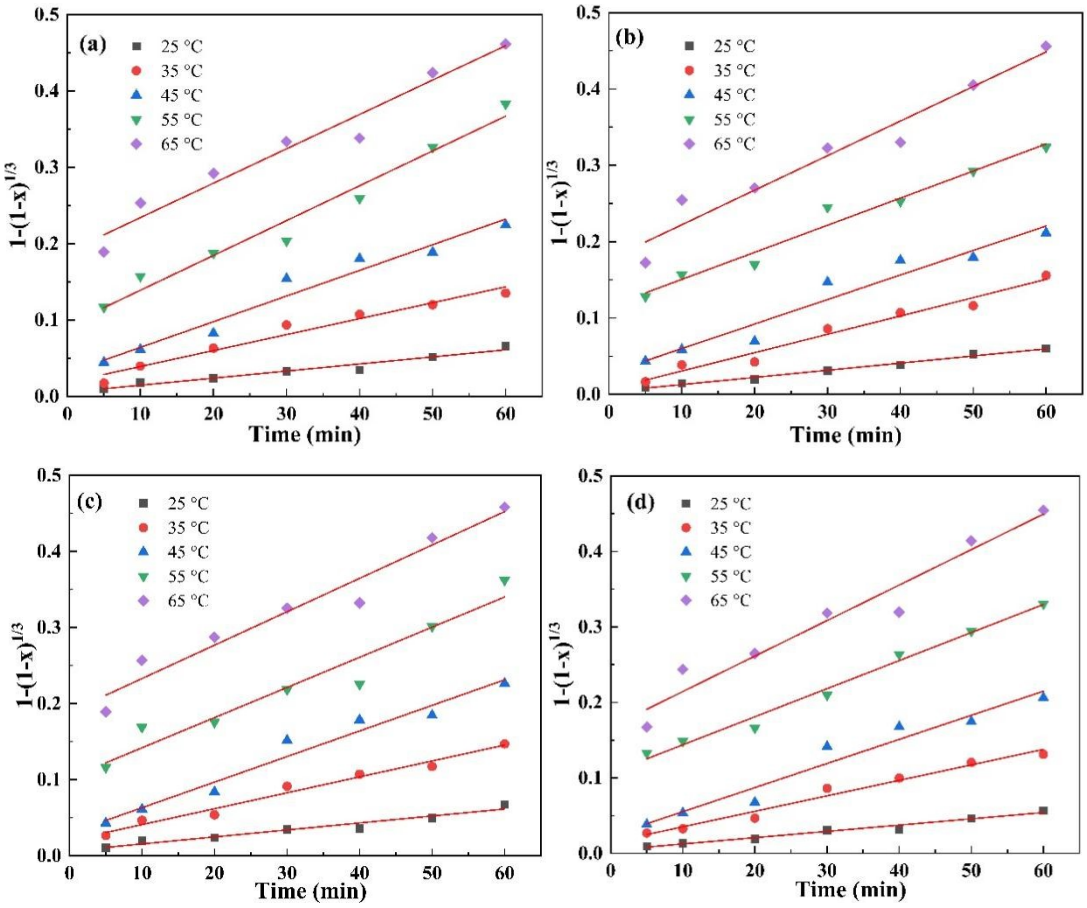

Fig. S11 Fitting results of surface chemical reaction control model for metal leaching efficiencies in H_2SO_4+H_2O_2 leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

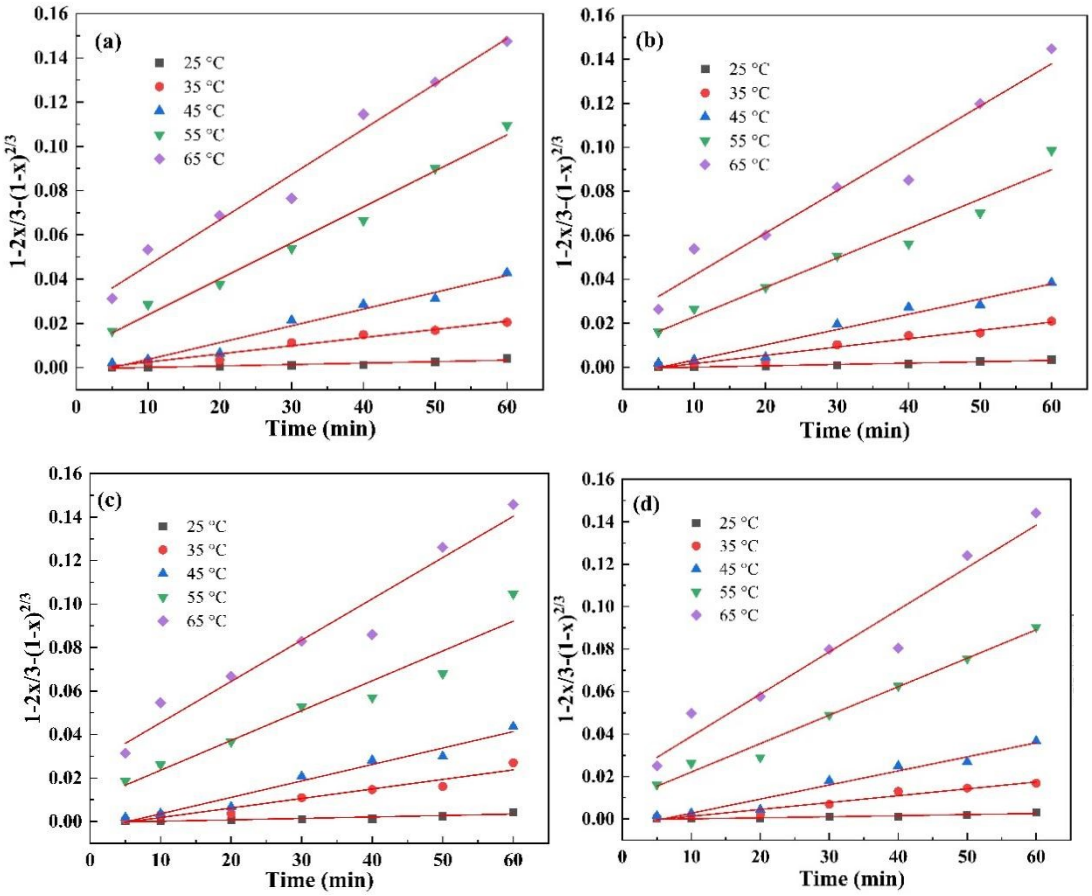

Fig. S12 Fitting results of internal diffusion control model for metal leaching efficiencies in H_2SO_4+H_2O_2 leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

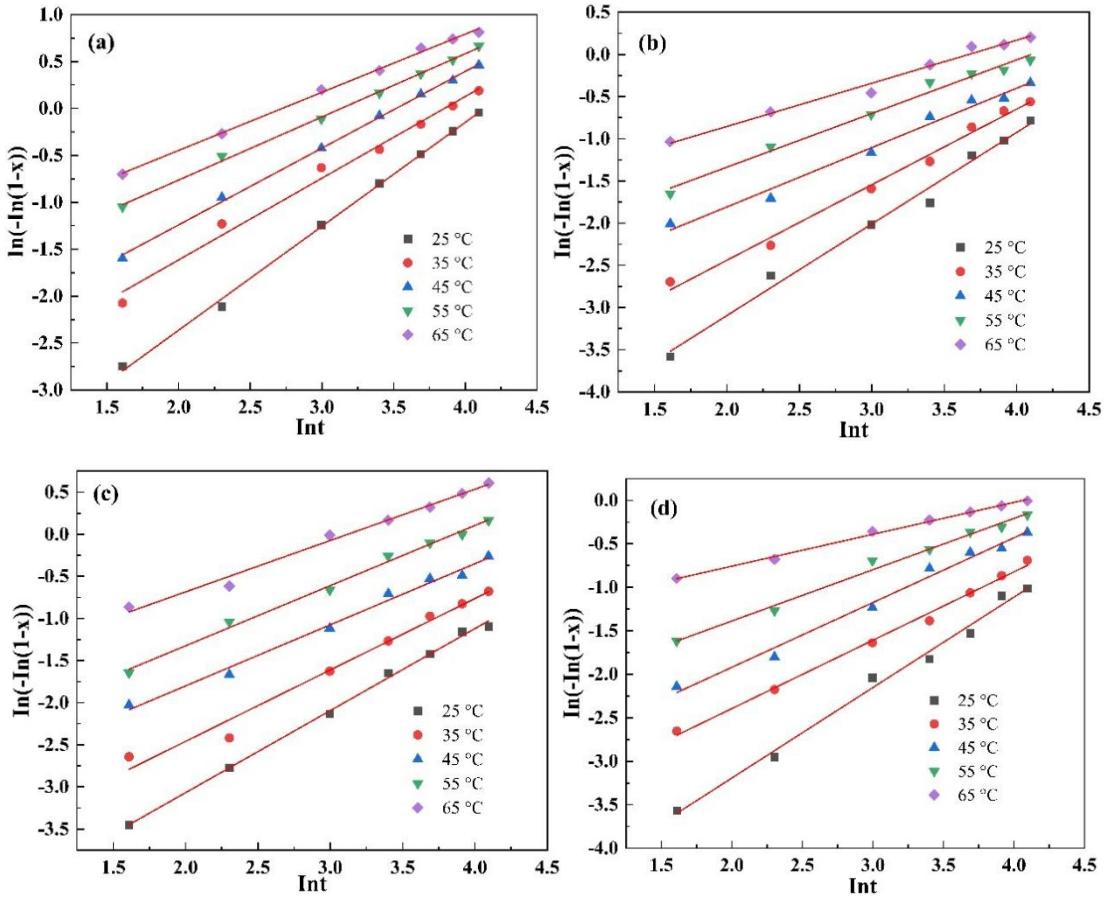

Fig. S13 Fitting results of Avrami equation for metal leaching efficiencies in H_2SO_4+H_2O_2 leaching system:(a) Li, (b)Ni, (c)Co, (d)Mn

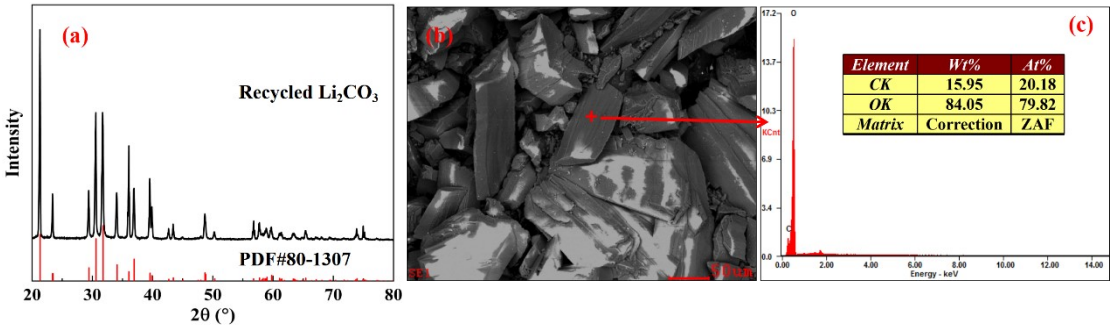

Fig. S14 Properties of the recovered lithium carbonate: (a) XRD of the recovered lithium carbonate, (b) SEM of the recovered lithium carbonate and (c) EDS of the recovered lithium carbonate

Table S1 Main chemical composition of the cathode materials

Composition	Li	Ni	Co	Mn	Al	Cu
Wt.%	6.97	30.74	12.69	18.71	0.64	0.02

Table S2 Content of GSH and GSSG in leaching solution

Composition	GSSG	GSH
	0.52 mol/L	0.52 mol/L

Table S3 Chemical composition of leachate under the optimal condition

Composition	Li	Ni	Co	Mn	GSSG	GSH
	3.49 g/L	15.34 g/L	6.31 g/L	9.3 g/L	0.26 mol/L	-

Table S4 Content of GSH and GSSG in solution

Composition	GSSG	GSH
	0.85 mol/L	-

Table S5 The results of regression analysis and variance analysis

Response value	Error source	P value	significance
Li	Leaching model	0.0011	Significant
	loss of fit	0.1213	Not significant
Ni	Leaching model	0.0036	Significant
	loss of fit	0.0937	Not significant
Co	Leaching model	0.0026	Significant
	loss of fit	0.0884	Not significant
Mn	Leaching model	0.0031	Significant
	loss of fit	0.1159	Not significant

Table S6 Fitting electrochemical parameters obtained from EIS

Materials	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
G-NCM	3.75	15.77	58.14
H-NCM	3.92	23.43	80.92

Table S7 The composition of the remaining solution after metal recovery

Composition	Li	Ni	Co	Mn	GSSG	GSH
	3.48 g/L	0.61 mg/L	0.33 mg/L	0.4 mg/L	0.26 mol/L	-

Table S8 The materials and energy consumption to dispose of 1 kg spent NCM cathode materials

	Items	Commodity price ($)	Dosage	Total
Leaching	Spent NCM cathode materials	31.06 for 1kg	1kg	31.06
	GSH	70 fo1 1kg	3.17kg	221.9
	H_2SO_4	0.08 for 1kg	1.96kg	0.16
	Energy cost	0.07 for 1 KW·h	0.09	0.006
Regeneration	Li_2CO_3	53.2 for 1kg	1kg	53.2
	Energy cost	0.07 for 1 KW·h	0.5	0.035
Cost				306.36

Calculation of costs:

At present, it is still in the stage of laboratory research, and there is no industrial data for reference. To simplify the cost calculation, only the costs of raw materials, chemical reagents and energy for the treatment of 1 kg spent NCM cathode material are considered. As all chemical reagents are provided by Chinese suppliers, the commodity price is converted from RMB (￥) to USD ($) according to the current exchange rate (December 2022).

(a)The cost of raw materials. The cost of spent NCM cathode materials is calculated at $31.06 /kg.

(b)The cost of reagents. According to the price and dosage of the reagents listed in Table S3, the cost of reagents for the recovery process is calculated as follow.

1- Leaching process:

$$\$70/kg * 3.17\ kg+\$0.08/kg * 1.96= \$222.05$$

2- Regeneration process:

$$\$53.2/kg * 1\ kg=\$53.2$$

(c)The cost of energy. According to Table S3, the cost of energy for the recovery process is calculated as follow.

$$\$0.07/\ KW{\cdot}h * 0.09\ KW{\cdot}h +\$0.07/kg * 0.5= \$0.0413$$

The total costs:

$$\$31.06+ \$222.05+\$53.2+\$0.0413 = \$306.36$$

Calculation of benefits and profits: When recycling of 1 kg of spent NCM523 cathode materials, 0.962 kg regenerated NCM523 can be obtained and 1 kg of NCM523 cathode material is 893.75$, the benefits and profits are calculated as follows.

Benefits:

$$893.75\$/kg*0.962\ kg=859.79\ \$$$

Profits:

$$\$859.79 - \$306.36 = 553.43\$$$

Table S9 The comparison of different methods for recycling of spent cathode material

Methods	Chemicals consumption	Energy Consumption	Leaching efficiencies	Ref.
Inorganic acid	2mol/L H_2SO_4,1-time theoretical dosage ofGSH,10:1 of LS	200rpm,65°C,1h	Over 99% of Li, Ni, Co and Mn	This work
	4mol/L H_2SO_4, 2 times theoretical dosage of H_2O_2, 8:1 of LS	500rpm,90°C, 2h	98% Ni,99% Co and 84% Mn	[1]
	1mol/L H_2SO_4, 0.075mol/L $NaHSO_3$, 20:1 of LS	95°C, 4h	96.7% Li, 96.4% Ni,91.6%Co,87.9%Mn	[2]
	3 mol/L H_2SO_4, 5% ethanol, 20:1 of LS	90°C, 3h	Over 99% of Li and Co	[3]
Organic acid	3.5 mol/L acetic acid, 40 g/L, 4% H_2O_2(volume fraction)	60°C, 90min	99.97 %Li,92.67 %Ni, 93.62 %Co,96.32 %Mn	[4]
	1.0 mol/L citric acid, 8% H_2O_2, S/L of 40:1,	70 min ,70 ℃	Over 99% of Li and Co	[5]
	0.075 mol/L benzenesulfonic acid, 3% H_2O_2, S/L of 15:1,	80 min ,90 ℃	99.58% Li, 96.53%Co	[6]
Alkaline leaching	1.5 mol/L NH_3H_2O, 1 mol/L $(NH_4)_2SO_3$ and NH_4HCO_3, S/L of 20:1,	180 min, 60 ℃	60.53% Li, 100%Ni, 80.99% Co, 100%Cu	[7]
	6 mol/L NH_3H_2O, 0.5 mol/L NH_4Cl, 0.5 mol/L, $(NH_4)_2SO_3$, S/L of 10:1,	30min, 150 ℃	90.3% Li, 100% Co, 98.3% Ni	[8]

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[8] S. Wang, C. Wang, F. Lai, F. Yan, Z. Zhang, Reduction-ammoniacal leaching to recycle lithium, cobalt, and nickel from spent lithium-ion batteries with a hydrothermal method: Effect of reductants and ammonium salts, Waste Manag, 102 (2020) 122-130.