Supporting Information for

Integrated recycling of valuable elements from spent $LiFePO_4$ batteries: a green closed-loop process

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Table S1 Concentrations of the elements in the filtrate obtained by the leaching process

Content	Li	Fe	P	Al
Concentration (mg/L)	3826	283	258	0.003

Table S2 Fitting parameters (R^2) of leaching Li using different models

Temperature	Model a	Model b	Model c	Model d
(°C)	R^2	R^2	R^2	R^2
25	0.9441	0.9489	0.9959	0.9989
35	0.9460	0.9432	0.9945	0.9964
45	0.8067	0.7936	0.8988	0.9733
55	0.8222	0.8096	0.8579	0.9669

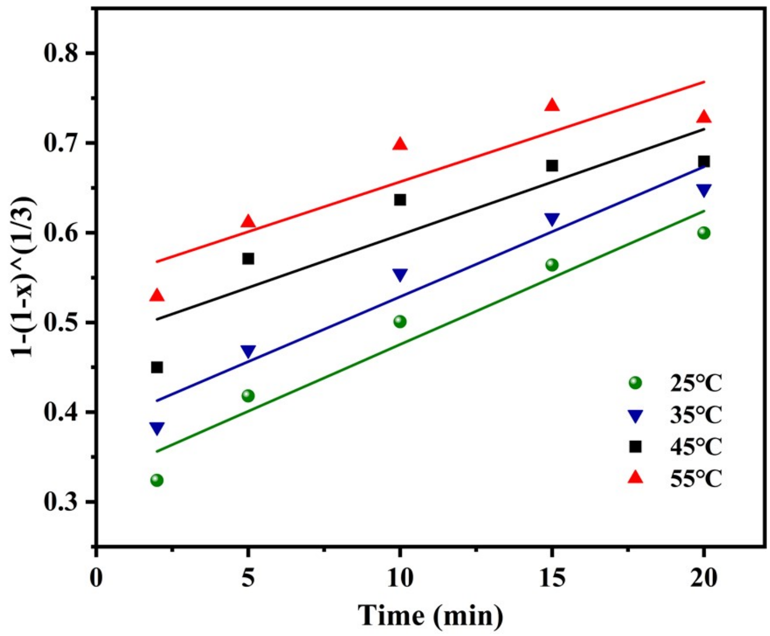

Fig. S1 Fitting results of Model a at various leaching temperatures for Li.

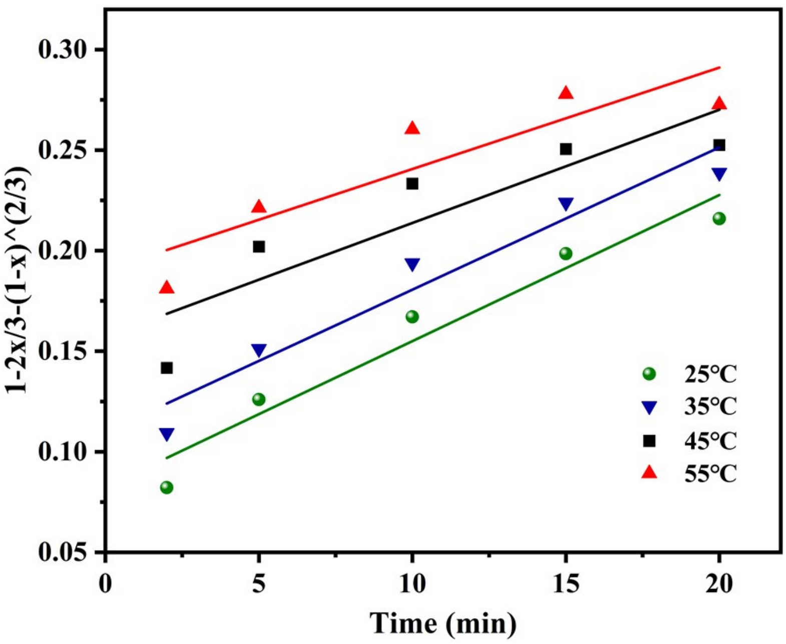

Fig. S2 Fitting results of the Model b at various leaching temperatures for Li.

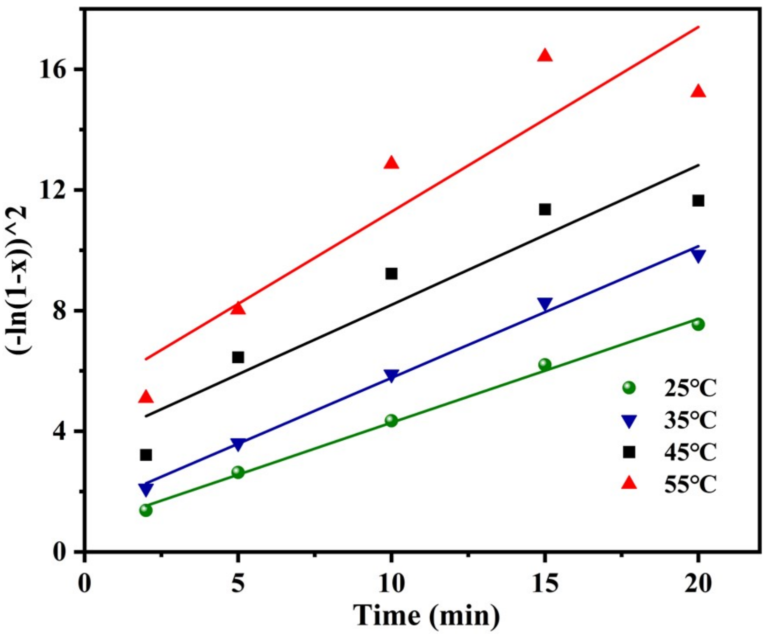

Fig. S3 Fitting results of the Model c at various leaching temperatures for Li.

Table S3. Equilibrium equations relative to the *E*-pH diagram of the Li-Fe-P-H_2O system at 298.15 K[1]

No.	Reactions	*E* vs pH equations
1	$2H^+ + 2e = H_2$	E =−0.0592 pH
2	$O_2 + 4e + 4H^+ = 2H_2O$	E = 1.229−0.0592 pH
3	$Fe^{3+} + e = Fe^{2+}$	E = 0.7696−0.0592 lg $[Fe^{2+}]/[Fe^{3+}]$
4	$FePO_4 \cdot 2H_2O + 3H^+ = Fe^{3+} + H_3PO_4 + 2H_2O$	pH =−3.482−1/3 lg $[Fe^{3+}][H_3PO_4]$
5	$FePO_4 \cdot 2H_2O + 3H^+ + e = Fe^{2+} + H_3PO_4 + 2H_2O$	E = 0.1515−0.0592 lg $[Fe^{2+}][H_3PO_4]$−0.1775 pH
6	$Fe_3(PO_4)_2 \cdot nH_2O + 6H^+ = 3Fe^{2+} + 2H_3PO_4 + nH_2O$	pH = 0.3654−1/3 lg $[H_3PO_4]$−1/2 lg $[Fe^{2+}]$
7	$3FePO_4 \cdot 2H_2O + 3e + 3H^+ = Fe_3(PO_4)_2 \cdot nH_2O + H_3PO_4 + (6-n) H_2O$	E = 0.1083−0.0197 lg $[H_3PO_4]$−0.0592 pH
8	$3LiFePO_4 + nH_2O + 3H^+ = Fe_3(PO_4)_2 \cdot nH_2O + 3Li^+ + H_3PO_4$	pH =1.1112−lg $[Li^+]$−1/3 lg $[H_3PO_4]$
9	$LiFePO_4 + 3H^+ = Fe^{2+} + Li^+ + H_3PO_4$	pH =0.6137−1/3 lg $[Li^+][Fe^{2+}][H_3PO_4]$
10	$FePO_4 \cdot 2H_2O + Li^+ + e = LiFePO_4 + 2H_2O$	E = 0.0426+0.0592 lg $[Li^+]$
11	$Li_3PO_4 + Fe(OH)_3 + 3H^+ = FePO_4 \cdot 2H_2O + 3Li^+ + H_2O$	pH = 6.0831−lg $[Li^+]$
12	$Fe(OH)_3 + Li_3PO_4 + 3H^+ + e = LiFePO_4 + 2Li^+ + 3H_2O$	E = 1.1224−0.1183 lg $[Li^+]$−0.1775 pH
13	$Fe(OH)_2 + Li_3PO_4 + 2H^+ = LiFePO_4 + 2H_2O + 2Li^+$	pH = 7.4167−lg $[Li^+]$
14	$Fe(OH)_3 + H^+ + e = Fe(OH)_2 + H_2O$	E = 0.2447−0.0592 pH

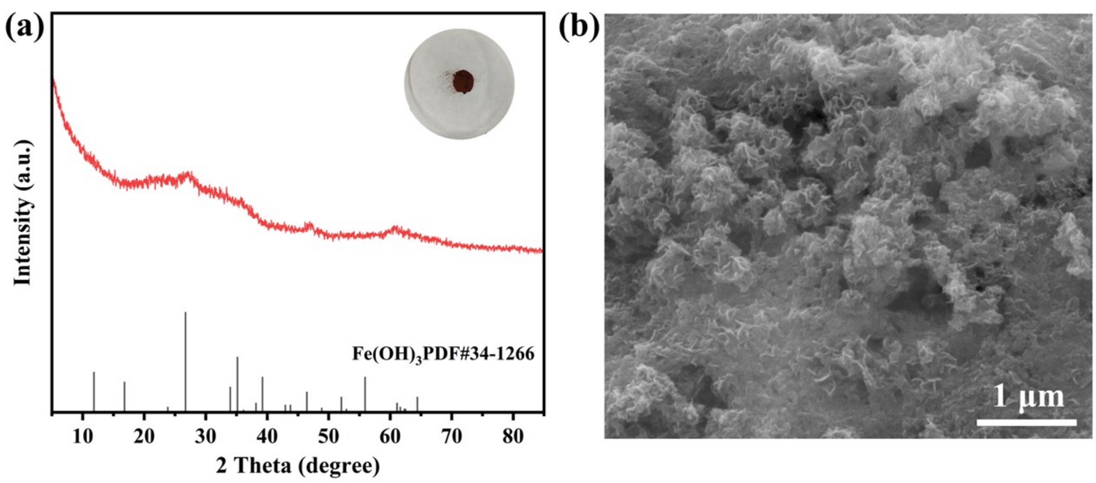

Fig. S4 (a) XRD pattern and (b) SEM image of the iron precipitation.

Table S4. Composition analysis of leaching residue under the optimized process

Content	$FePO_4$	Fe	Li	P	Al
Composition (wt.%)	99.78	39.56	0.24	19.67	0.01

Table S5. Purity analysis of the final product for Li_2CO_3 under the optimized process

Content	Li_2CO_3	Na	Fe	P	Al
Composition (wt.%)	99.63	0.0238	0.0001	0.0105	0.001

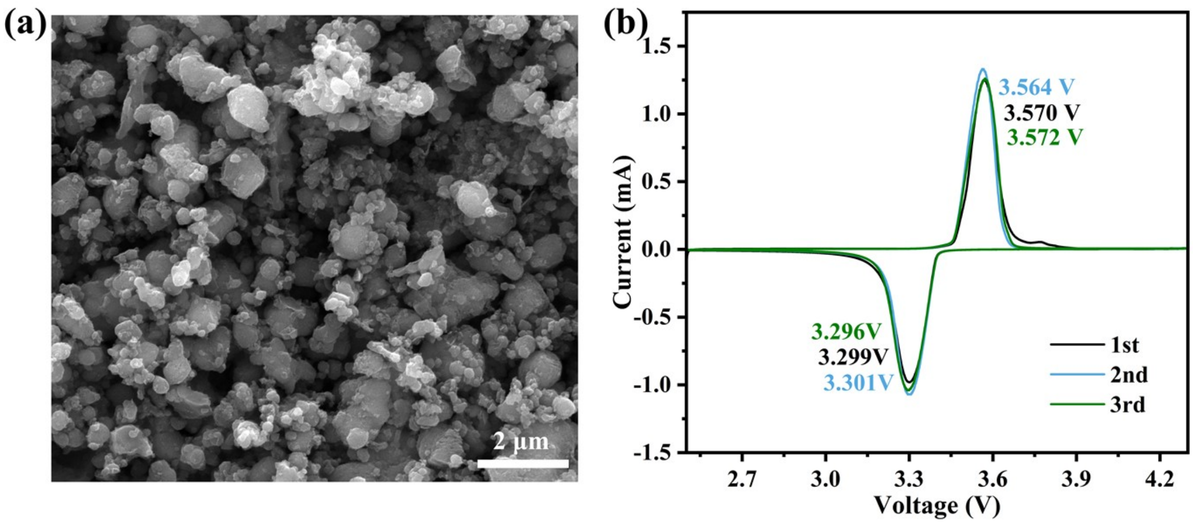

Fig. S5 (a) SEM image of RLFP, (b) cyclic voltammogram of RLFP at 0.1 mv s^{-1}.

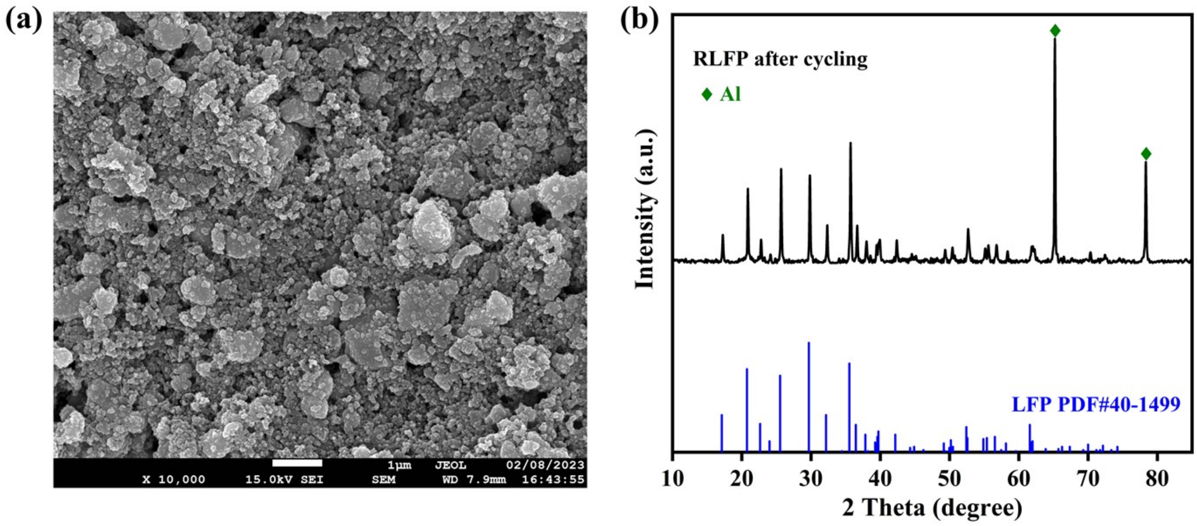

Fig. S6 (a) SEM and (b) XRD of RLFP cathode sheet after cycling.

Table S6. The cost and profit to dispose of 1 kg spent $LiFePO_4$ cathode power in China (exchange rate: 1 \$ = 7.0338 CNY, accessed June 12, 2023).

	Chemical	Price	Dosage	Total
Consumption	SLFP	6.823 \$/kg	1.0 kg	6.823 \$
	H_2O_2(30 wt%)	0.138\$/L	0.4 L	0.055 \$
	DL-H_2Ma	2.133 \$/kg	0.322 kg	0.687 \$
	NaOH	0.427\$/kg	0.004 kg	0.0017 \$
	Na_2CO_3	0.355\$/kg	0.284 kg	0.101 \$
	Electricity	0.142 \$/kw·h^{-1}	2.685 kw·h	0.381 \$
	Water	0.06 \$/t	0.3 t	0.018 \$
	Labor	200 \$/t	0.001 t	0.2 \$
Total	8.267\$			
	Chemical	Price	Dosage	Total
Product	$FePO_4$	2.133 \$/kg	0.730 kg	1.557 \$
	Li_3PO_4	4.976 \$/kg	0.022 kg	0.109 \$
	Li_2CO_3	42.651 \$/kg	0.195 kg	8.317 \$
Total	9.983 \$			
Profit	1.716 \$			

As listed in Table S8, based on 1.0 kg spent $LiFePO_4$ cathode powders, the total costs and profits in the laboratory-scale recycling process were calculated in detail. Chemicals such as H_2O_2 and DL-malic acid were consumed in the whole recycling process, and the costs of water, electricity, and labour treatment are also taken into account in the economic analysis. It is estimated that 730 g $FePO_4$, 22 g Li_3PO_4, and 195 g Li_2CO_3 could be obtained from the treatment of 1.0 kg waste $LiFePO_4$ cathode materials. Ultimately, the profit of recycling 1.0 kg spent $LiFePO_4$ cathode powders is \$1.716.

Table S7. A comparison of different recovery processes for SLFP.

Oxidant	Condition	Leaching efficiency	Reagent cost	Energy and equipment cost	Characteristics	Ref.
n (DL-malic acid/Li) = 0.435, 4 vol.% H_2O_2	100 g/L, 25°C, 30 min	99.12% Li, 0.81% Fe, 1.42% P	Low	Low	High efficiency and green process	This work
0.3 M H_2SO_4, n (H_2O_2/Li) = 2.07	60°C, 2 h	97% Li, 0.027% Fe, 1.95% P	High	High	High selectivity while large reagent consumption	[2]
2.5 M H_2SO_4, High-Temperature Oxidation	60°C, 4 h, 100 g/L	97% Li, 0.027% Fe	High	High	High cost and harsh conditions	[3]
n (HCl /Li) = 0.8, n (NaClO/Li) = 1	60min, 50-80°C, 1-4 g/mL	97% Li, < 2% Fe.	Low	High	High leaching efficiency while harsh conditions	[4]
n ($Fe_2(SO_4)_3$/LFP =1:6), 0.6 mL/g H_2O_2	400 g/L, 60°C, 30 min	96.5% Li	Low	Low	Selective leaching while low leaching efficiency	[5]
1.0 M HCOOH, 5 vol. % H_2O_2	30 min, 10 g/L, 30°C	97.92 % Li, <0.5% Fe/P	High	High	High efficiency while high cost	[6]
100% Lemon juice, 6 vol% H_2O_2	67 g/L, 60 min	94.83% Li, 4.05% Fe, 0.84% P	High	Low	Green process while low selectivity	[7]
4 M MSA, 18 vol. % H_2O_2	80 g/L, room temperature, 90 min	94% Li, 95% Fe	High	Low	Mild reaction condition while non-selective leaching	[8]
0.8 M CH_3COOH, 6 vol% H_2O_2	120 g/L, 50°C, 30 min	95.05% Li, 0.93% Fe	Low	Low	Mild reaction condition while low leaching efficiency	[9]
Air (flow rate of 600 mL· min^{-1})	pH=3.5, 25 °C, 10 mL·g^{-1}, 5 h	99.3% Li, 0.02% Fe/P	Low	High	High selectivity while complex operation	[1]
15 vol. % H_2O_2	30 min, 50 °C, 10 g/L	97.6% Li	Low	High	High efficiency while high cost	[10]
n ($Na_2S_2O_8$/LFP) =1.05	300 g/L, 25°C, 20 min	99% of Li	Low	Low	High efficiency and low cost	[11]

n $((NH_4)_2S_2O_8/LFP)$ = 1.4	30 min, 30°C, 50 g/L	98.1% Li, <1% Fe/ Al	High	Low	High efficiency while high cost	[12]

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