

Supplementary information for
Closed-loop recovery of waste lithium iron phosphate by safe and
environmentally friendly nitric acid selective leaching with bipolar membrane

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1. Supplemental Figures

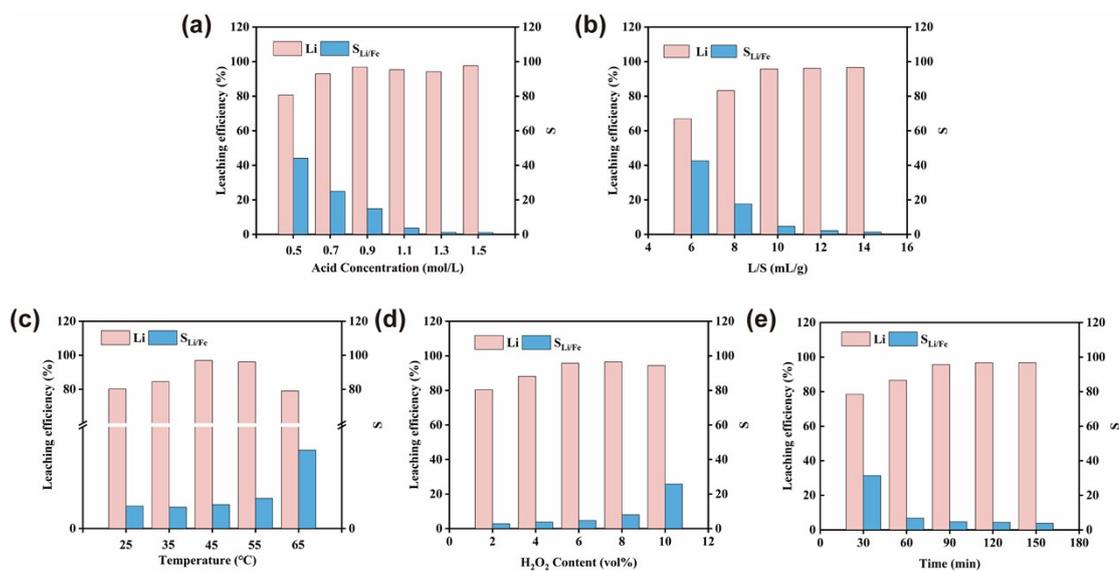


Fig. S1. (a-f) Variations in the selectivity coefficient (S) of lithium relative to iron under different leaching conditions (as shown in Fig. 3).

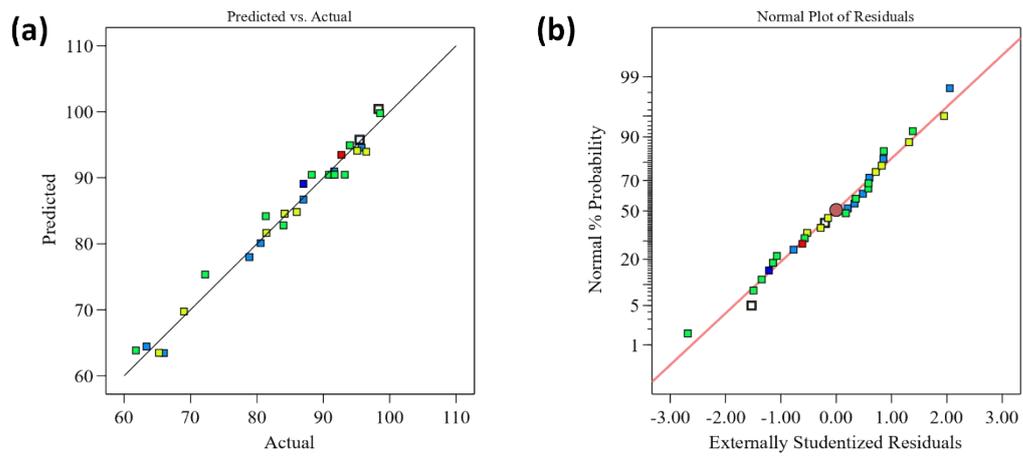


Fig. S2. (a) Comparison of theoretical values obtained by response surface method simulation and actual experimental values and (b) Normal probability plot of residuals.

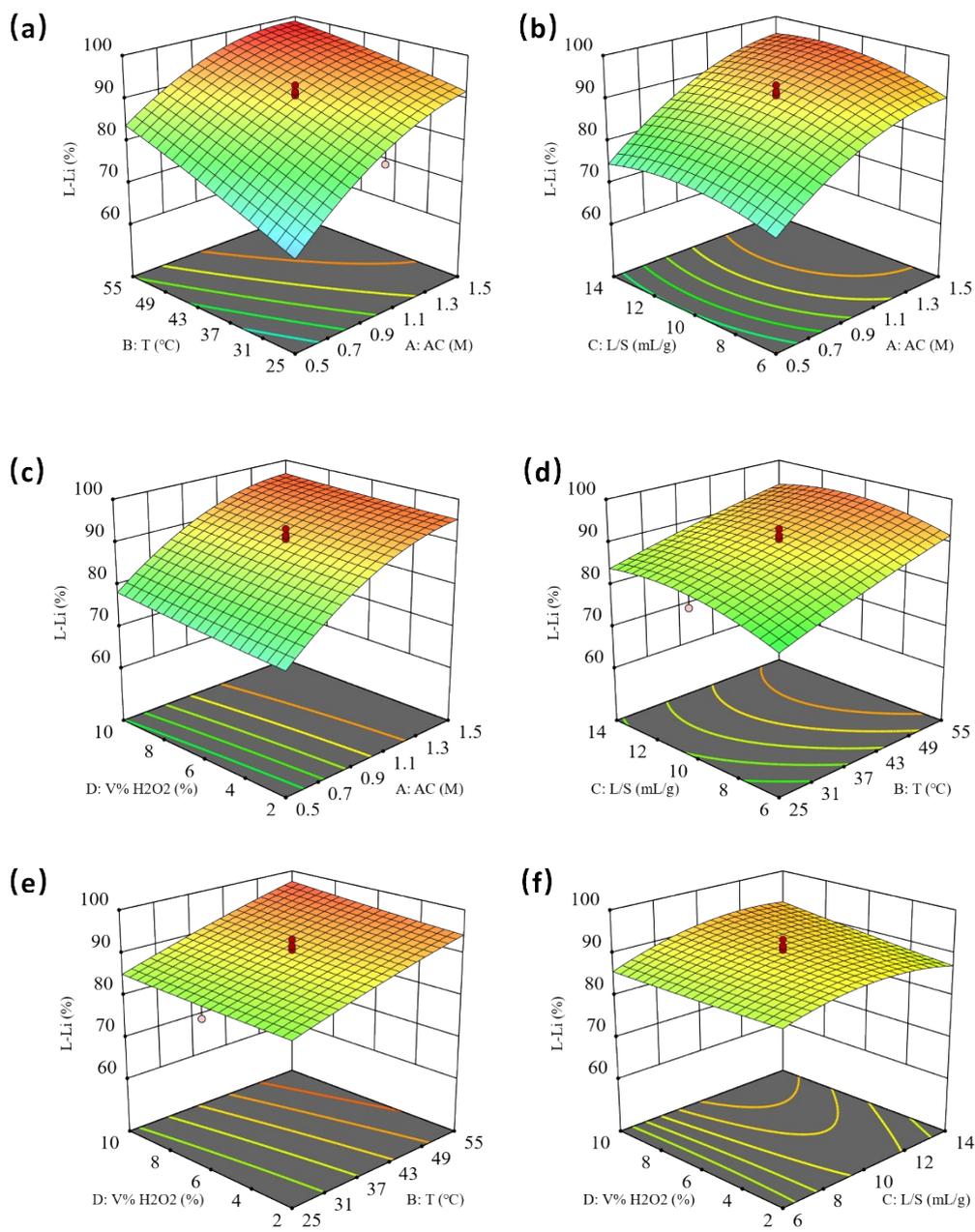


Fig. S3. 3D response surface plot: (a-f) The effect of interaction between various factors on lithium ion leaching rate.

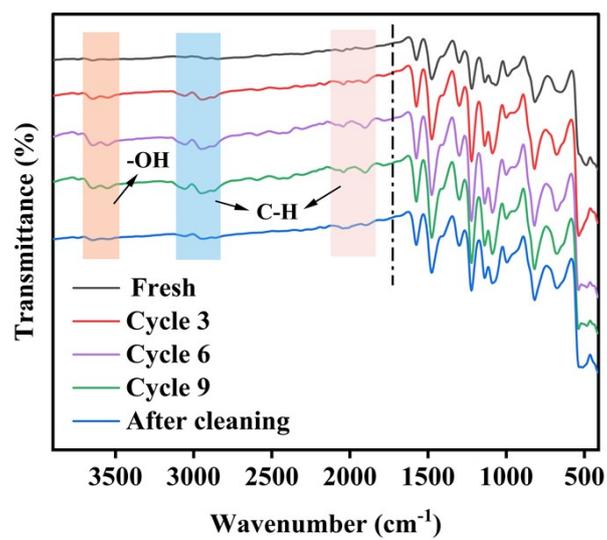


Fig. S4. CEM FT-IR spectra over multiple cycles.

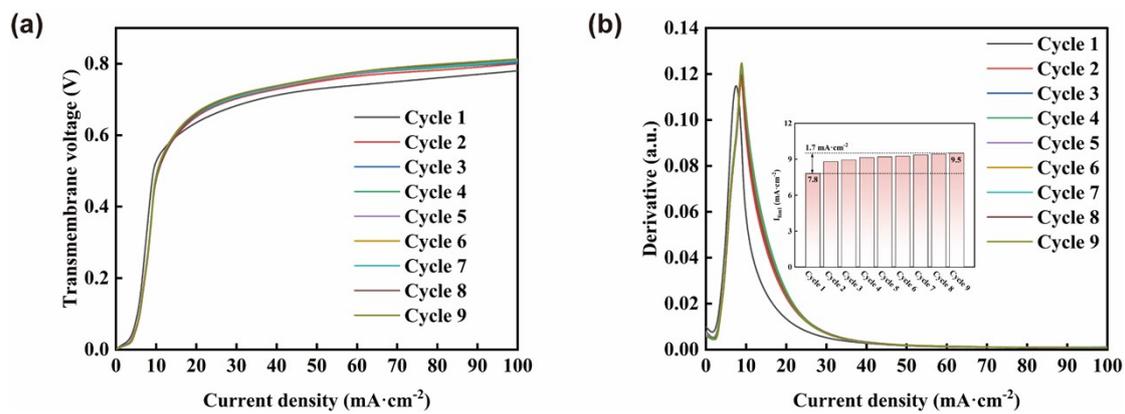
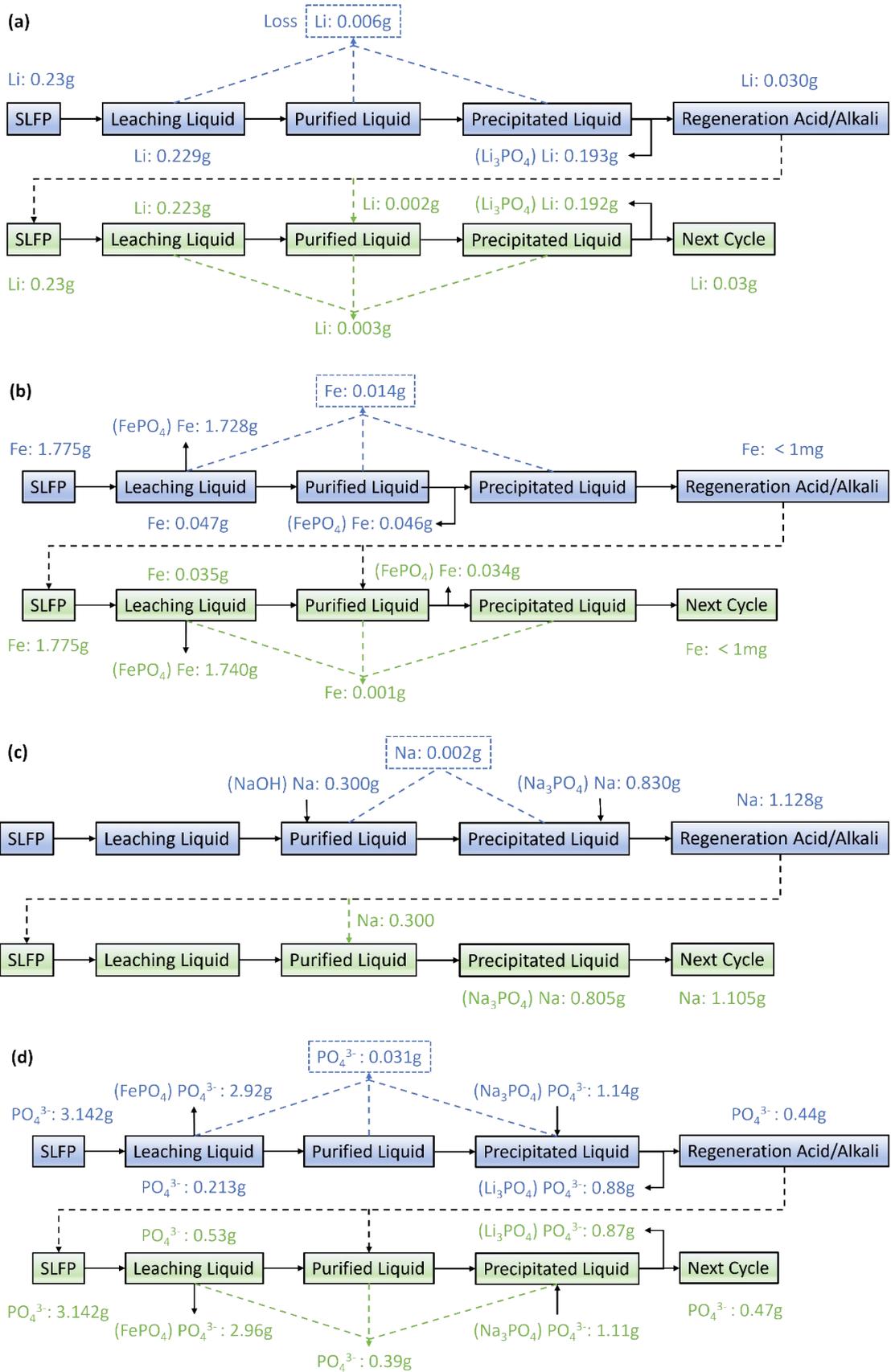


Fig. S5. (a) Bipolar membrane I-V curves ($0\text{--}100\text{ mA}\cdot\text{cm}^{-2}$); (b) Corresponding derivative curves.



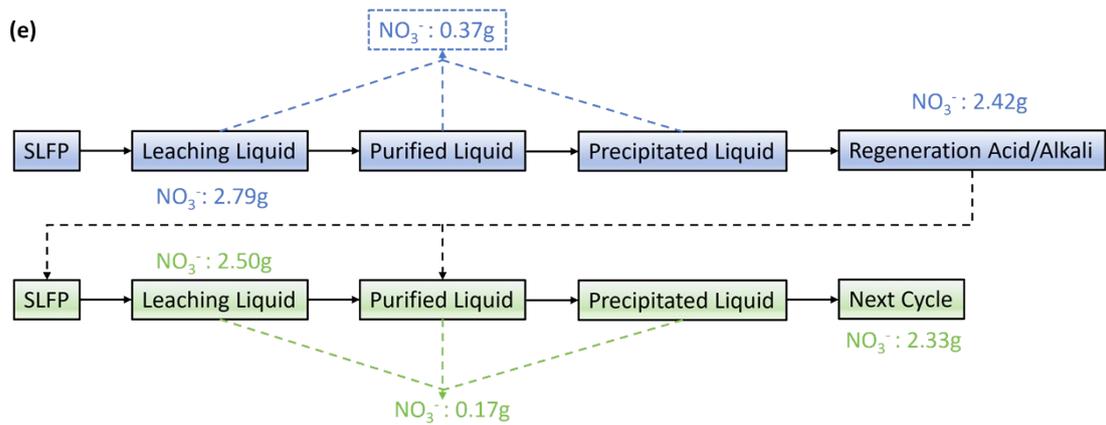


Fig. S6. Material balance of individual ions (Li, Na, Fe, PO₄³⁻, NO₃⁻) during a single cycle.

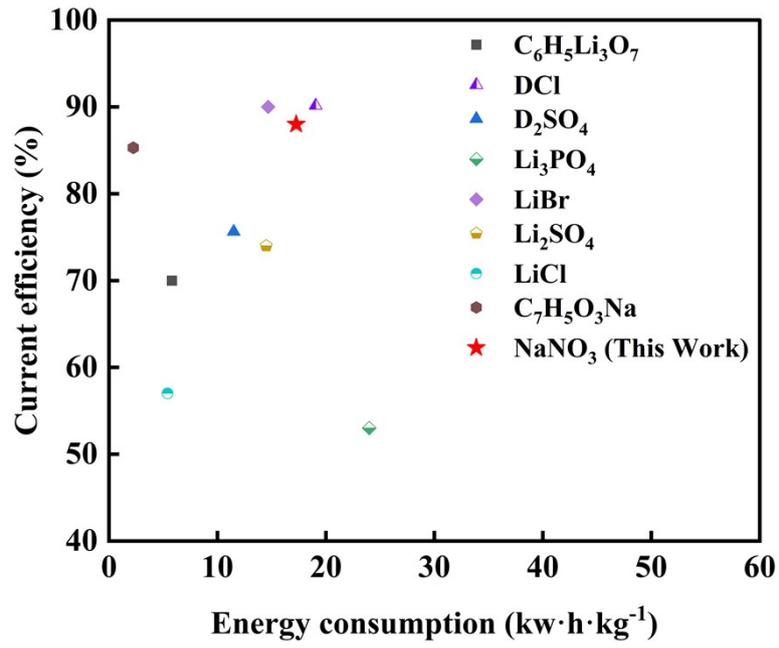


Fig. S7. Comparison of energy consumption and current efficiency of the BMED system under different feed solution compositions.

2. Supplemental Tables

Table S1. Content of elements in SLFP powder.

Main components (%)				Content of impurity metal ions (%)							
C	Li	Fe	P	Ca	Na	Mg	Cr	Mn	Ni	Cu	Zn
0.9~	4.3	34.5	19.5	≤	≤	≤	≤	≤	≤	≤	≤
1.4	±0	±	±	0.03	0.03	0.03	0.015	0.01	0.01	0.005	0.005
	.3	1.0	1.0								

Table S2. Parameters of each ion in the salt chamber (200ml).

ion	Na ⁺	Li ⁺	NO ₃ ⁻	PO ₄ ³⁻
Concentration (g·L ⁻¹)	5.643	0.149	12.101	2.260

Table S3. Response surface experiment results.

std	Run	Factor 1 A: AC mol·L ⁻¹	Factor 2 B: T °C	Factor 3 C: L/S mL·g ⁻¹	Factor 4 D: H ₂ O ₂ vol% %	Response 1 Leaching Li %	Response 2 Leaching Fe %
1	29	0.5	25	6	2	66	6.5
2	4	1.5	25	6	2	87	92.7
3	10	0.5	55	6	2	80.6	9.8
4	25	1.5	55	6	2	95.8	83.4
5	19	0.5	25	14	2	63.4	43.3
6	8	1.5	25	14	2	91.7	89
7	28	0.5	55	14	2	78.9	40.6
8	15	1.5	55	14	2	95.5	73.8
9	7	0.5	25	6	10	65.3	1.8
10	23	1.5	25	6	10	84.2	22.3
11	18	0.5	55	6	10	81.4	3.7
12	22	1.5	55	6	10	96.5	37.5
13	16	0.5	25	14	10	69	7.1
14	11	1.5	25	14	10	95.1	20.4
15	12	0.5	55	14	10	86	20.6
16	30	1.5	55	14	10	98.3	67.2
17	26	0.2	40	10	6	61.8	2.4
18	20	1.8	40	10	6	94	90.6
19	5	1	25	10	6	81.3	1.3
20	6	1	70	10	6	98.6	77.4
21	1	1	40	2	6	72.2	0.3
22	24	1	40	18	6	84	83
23	27	1	40	10	0	87	98.4
24	9	1	40	10	14	92.7	3.7
25	3	1	40	10	6	91.2	16.6
26	21	1	40	10	6	90.8	17.3
27	2	1	40	10	6	88.3	16.5
28	14	1	40	10	6	91.7	23.2
29	13	1	40	10	6	93.2	19.8
30	17	1	40	10	6	91.7	20.4

Table S4. Equilibrium equation of E-pH in Li-Fe-P-H₂O system at 298.15K.

No.	Reactions	E vs pH equations
1	$2\text{H}^+ + 2\text{e} = \text{H}_2$	$E = -0.0592\text{pH}$
2	$\text{O}_2 + 4\text{e} + 4\text{H}^+ = 2\text{H}_2\text{O}$	$E = 1.229 - 0.0592\text{pH}$
3	$\text{Fe}^{3+} + \text{e} = \text{Fe}^{2+}$	$E = 0.7696 - 0.0592 \lg[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$
4	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} + 3\text{H}^+ = \text{Fe}^{3+} + \text{H}_3\text{PO}_4 + 2\text{H}_2\text{O}$	$\text{pH} = -3.482 - 1/3 \lg[\text{Fe}^{3+}][\text{H}_3\text{PO}_4]$
5	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} + 3\text{H}^+ + \text{e} = \text{Fe}^{2+} + \text{H}_3\text{PO}_4 + 2\text{H}_2\text{O}$	$E = 0.1515 - 0.0592 \lg[\text{Fe}^{2+}][\text{H}_3\text{PO}_4] - 0.1775 \text{pH}$
6	$\text{Fe}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O} + 6\text{H}^+ = 3\text{Fe}^{2+} + 2\text{H}_3\text{PO}_4 + n\text{H}_2\text{O}$	$\text{pH} = 0.3654 - 1/3 \lg[\text{H}_3\text{PO}_4] - 1/2 \lg[\text{Fe}^{2+}]$
7	$3\text{FePO}_4 \cdot 2\text{H}_2\text{O} + 3\text{e} + 3\text{H}^+ = \text{Fe}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O} + \text{H}_3\text{PO}_4 + (6-n)\text{H}_2\text{O}$	$E = 0.1083 - 0.0197 \lg[\text{H}_3\text{PO}_4] - 0.0592\text{pH}$
8	$3\text{LiFePO}_4 + n\text{H}_2\text{O} + 3\text{H}^+ = \text{Fe}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O} + 3\text{Li}^+ + \text{H}_3\text{PO}_4$	$\text{pH} = 1.1112 - \lg[\text{Li}^+] - 1/3 \lg[\text{H}_3\text{PO}_4]$
9	$\text{LiFePO}_4 + 3\text{H}^+ = \text{Fe}^{2+} + \text{Li}^+ + \text{H}_3\text{PO}_4$	$\text{pH} = 0.6137 - 1/3 \lg[\text{Li}^+][\text{Fe}^{2+}][\text{H}_3\text{PO}_4]$
10	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} + \text{Li}^+ + \text{e} = \text{LiFePO}_4 + 2\text{H}_2\text{O}$	$E = 0.0426 + 0.0592 \lg[\text{Li}^+]$
11	$\text{Li}_3\text{PO}_4 + \text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{FePO}_4 \cdot 2\text{H}_2\text{O} + 3\text{Li}^+ + \text{H}_2\text{O}$	$\text{pH} = 6.0831 - \lg[\text{Li}^+]$
12	$\text{Fe}(\text{OH})_3 + \text{Li}_3\text{PO}_4 + 3\text{H}^+ + \text{e} = \text{LiFePO}_4 + 2\text{Li}^+ + 3\text{H}_2\text{O}$	$E = 1.1224 - 0.1183 \lg[\text{Li}^+] - 0.1775\text{pH}$
13	$\text{Fe}(\text{OH})_2 + \text{Li}_3\text{PO}_4 + 2\text{H}^+ = \text{LiFePO}_4 + 2\text{H}_2\text{O} + 2\text{Li}^+$	$\text{pH} = 7.4167 - \lg[\text{Li}^+]$
14	$\text{Fe}(\text{OH})_3 + \text{H}^+ + \text{e} = \text{Fe}(\text{OH})_2 + \text{H}_2\text{O}$	$E = 0.2447 - 0.0592\text{pH}$

Table S5. Kinetics leaching results at different temperatures and times.

Temperature (°C)	Kinetics fitting data				
	30	60	90	120	150
25	0.6727	0.7354	0.8024	0.8321	0.8533
35	0.7537	0.8292	0.8747	0.892	0.9035
45	0.8025	0.8736	0.9152	0.93	0.941
55	0.8523	0.915	0.9513	0.9633	0.9689

Table S6. Kinetics fitting data of $Y=x$ vs. time at different temperatures.

Temperature (°C)	Kinetics fitting data				
	30	60	90	120	150
25	0.6727	0.0977	0.8024	0.8321	0.8533
35	0.7537	0.8292	0.8747	0.892	0.9035
45	0.8025	0.8736	0.9152	0.9300	0.9410
55	0.8523	0.9150	0.9313	0.9633	0.9689

Table S7. Kinetics fitting data of $Y=1-2/3x-(1-x)^{2/3}$ vs. time at different temperatures.

Temperature (°C)	Kinetics fitting data				
	30	60	90	120	150
Time(min)					
25	0.0766	0.7354	0.1258	0.1409	0.1530
35	0.1052	0.1394	0.1665	0.1785	0.1872
45	0.1258	0.1658	0.1970	0.2099	0.2210
55	0.1523	0.1967	0.2114	0.2474	0.2552

Table S8. Kinetics fitting data of $Y=1-(1-x)^{1/3}$ vs. time at different temperature.

Temperature (°C)	Kinetics fitting data				
Time(min)	30	60	90	120	150
25	0.3108	0.3581	0.4176	0.4483	0.4726
35	0.3736	0.4452	0.4996	0.5238	0.5412
45	0.4176	0.4982	0.5609	0.5876	0.6106
55	0.4714	0.5604	0.5904	0.6677	0.6855

Principles and model of leaching kinetics

Based on the classical shrinking core model, the leaching kinetics of LiFePO_4 were analyzed in this work. This model is suitable for describing the dissolution process of solid particles under the action of a leaching agent, with the main reaction steps including:

- (1) external diffusion of the leaching agent to the particle surface;
- (2) internal diffusion of the leaching agent through the liquid film;
- (3) chemical reaction between the leaching agent and the particle surface.

The rate-controlling step can be identified by fitting the experimental data to the following equations:

External-diffusion control:

$$x=k_1t \quad (6)$$

Internal-diffusion control:

$$1-2/3x-(1-x)^{2/3}=k_2t \quad (7)$$

Chemical-reaction control:

$$1-(1-x)^{1/3}=k_3t \quad (8)$$

Where x is the lithium leaching efficiency, k_1 , k_2 and k_3 are the apparent rate constants, and t is time.

The apparent activation energy (E_a) was further calculated using the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \quad (9)$$

Where k is the rate constant, A is the frequency factor, E_a is the apparent activation energy, R is the gas constant of $8.314\text{J}/(\text{mol K})$ and T is the thermodynamic temperature (K).

Table S9. Single-cycle pathway (Leaching–Recovery–Spent solution regeneration–Acid/Alkali reuse).

Cycle number	Acid Chamber (mg/L)		Alkali Chamber (mg/L)	
	NO ₃ ⁻	PO ₄ ³⁻	Na ⁺	Li ⁺
Fresh	23704	4171	11240.5	296.8
1	22690	4305.9	11294.5	288.4
2	22209	4409.4	10745.1	362.3
3	22250	4271.9	10822.7	273.5
4	22319	4239.8	10708.5	308.1
5	22450	4157.3	10624.9	321.9
6	22310	4097.6	10625.0	305.0
7	22287	4106.9	10835.6	322.2
8	22276	4001.1	10660.6	275.5
9	22100	4110.6	10677.7	325.7

Table S10. Cost and profit of processing 1kg SLFP powder in HNO₃/H₂O₂ mixed leaching system (1\$=7.1696 RMB).

	Category	Price	Dosage	Total
Consumption	SLFP	1.62 \$/kg	1 kg	1.62 \$
	HNO ₃	0.14 \$/L	0.59 L	0.083 \$
	H ₂ O ₂ (30%)	0.14 \$/L	0.4 L	0.056 \$
	NaOH	0.427 \$/kg	0.06 kg	0.03 \$
	Na ₃ PO ₄	0.418 \$/kg	0.236 kg	0.1 \$
	Electricity	0.07 \$/kwh	2.64 kwh	0.18 \$
	Water	0.06 \$/t	0.092t	0.006 \$
	Labor	0.11 \$/kg	1	0.11
Total		2.08 \$		
Product	FePO ₄	2.13 \$/kg	0.93 kg	1.98 \$
	Li ₃ PO ₄	5.02 \$/kg	0.22 kg	1.1 \$
Regeneration Acid/Alkali		0.234 \$		
Total		3.314 \$		
Profit		1.234 \$		

Table S11. Comparison of Li/Fe recovery rates in the leaching stage with other reported works.

Process object	Main product (purity)	Recovery efficiency	Effluent	Ref.
Spent LiFePO ₄	Li ₂ CO ₃ (99.9%) FePO ₄	Li:(85.05%)	Yes	[14]
Spent LiFePO ₄	Li ₃ PO ₄ (99%) FePO ₄	Li:(99.5%)	Yes	[15]
Spent LiFePO ₄	FePO ₄ Li ₂ CO ₃ (99.56%)	Fe:(99.99%) Li:(89.13%)	Yes	[16]
Spent LiFePO ₄	FePO ₄ ·2H ₂ O Li ₃ PO ₄	Fe:(93.05%) Li:(82.55%)	Yes	[17]
Spent LiFePO ₄	Li ₃ PO ₄ (99.85%) FePO ₄	Li: (One-time recovery rate 87%) Fe:(>99%)	No	This work

Table S12. Profit comparison of the HNO₃/H₂O₂ leaching system versus alternative hydrometallurgical routes

Process object	Oxidant	Main product	Profit/\$	Ref.
1 kg of LFP	H ₂ SO ₄ /Air	Li ₂ CO ₃ /FePO ₄ ·2H ₂ O	1.203	[1]
1 kg of LFP	(NH ₄) S ₂ O ₈	Li ₂ CO ₃ /FePO ₄	0.834	[2]
1 kg of LFP	DL-malic acid/H ₂ O ₂	Li ₂ CO ₃ /Li ₃ PO ₄ /FePO ₄	1.716	[3]
1 kg of LFP	CH ₃ COOH/H ₂ O ₂	Li ₂ CO ₃ /FePO ₄	0.646	[4]
1 kg of LFP	MSA/TsOH	Li ₂ CO ₃ /FePO ₄	1.130	[5]
1 kg of LFP	H ₂ SO ₄ /Air	Li ₂ CO ₃ /FePO ₄	2.030	[6]
1 kg of LFP	H ₂ SO ₄ /FeSO ₄	LiFePO ₄	1.297	[7]
1 kg of LFP	HNO ₃ /H ₂ O ₂	Li ₃ PO ₄ /FePO ₄	1.234	This work

Table S13. Economic analysis of BMED equipment.

Parameters	BMED process
Feed volume (L)	0.2
Feed salt concentration (%)	4
Current density ($\text{mA}\cdot\text{cm}^{-2}$)	40
Batch experiment time (h)	10
Effective each membrane area (cm^2)	7.065
Energy consumption ($\text{kWh}\cdot\text{kg}^{-1}\cdot\text{NaOH}$)	17.26
Treatment capacity ($\text{kg}\cdot\text{NaOH}\cdot\text{year}^{-1}$)	1.97
Price of bipolar membrane ($\text{\$}\cdot\text{m}^{-2}$)	800
Price of mono membrane ($\text{\$}\cdot\text{m}^{-2}$)	200
Membrane lifetime and amortization of the peripheral equipment (year)	3
Electricity charge ($\text{\$}\cdot\text{kW}\cdot\text{h}^{-1}$)	0.0684
Membrane cost (\$)	1.413
Apparatus cost (\$)	2.12
Peripheral equipment cost (\$)	3.18
Total investment cost (\$)	6.713
Amortization ($\text{\$}\cdot\text{year}^{-1}$)	2.237
Maintenance ($\text{\$}\cdot\text{year}^{-1}$)	0.671
Total fixed cost ($\text{\$}\cdot\text{year}^{-1}$)	2.9
Total fixed cost ($\text{\$}\cdot\text{kg}^{-1}\cdot\text{NaOH}$)	1.472
Energy cost ($\text{\$}\cdot\text{kg}^{-1}\cdot\text{NaOH}$)	1.18
Total process cost ($\text{\$}\cdot\text{kg}^{-1}\cdot\text{NaOH}$)	2.652

The BMED system operates for 8,720 h per year. The stack cost is 1.5 times that of the membrane modules, while the peripheral equipment cost is 1.5 times that of the stack. The service life of the membrane modules and the depreciation period of the peripheral equipment are both set at three years. The maintenance costs account for 10% of the total investment cost.

Table S14. Performance and cost comparison between the BMED process and other major recycling processes.

Treatment	Main product	Recycling percentage	Product purity	Cost/\$·kg ⁻¹ ·NaOH/LiOH	Ref.
Simulated LiFePO ₄ leaching solution	LiOH	85%	99%	—	[8]
NaCl solution	NaOH	96%	—	1.230	[9]
Li ₃ PO ₄ solution	LiOH	99%	—	2.941	[10]
Salt lake solution	LiOH	57.7%	99%	—	[11]
Simulated leaching solution	LiOH	82.34%	99%	—	[12]
LiBr	LiOH	99%	—	2.243	[13]
LiFePO ₄ leaching solution	NaOH	>95%	95%	2.652	This work

Table S15. Sensitivity analysis (increment: +20%).

Parameters	Fixed cost (\$·kg ⁻¹ ·NaOH)	Energy cost (\$·kg ⁻¹ ·NaOH)	Total process cost (\$·kg ⁻¹ ·NaOH)	Rate of change (%)	Sensitivity coefficient
Energy	1.543	1.416	2.959	+8.67	0.433
cost	1.543	0.944	2.487	-8.67	0.433
Electricity	1.543	1.416	2.959	+8.67	0.433
charge	1.543	0.944	2.487	-8.67	0.433
Price of bipolar membrane	1.587	1.180	2.767	+1.62	0.081
Price of mono membrane	1.507	1.180	2.687	-1.32	0.066
Price of mono membrane	1.557	1.180	2.737	+0.51	0.026
Price of mono membrane	1.537	1.180	2.717	-0.22	0.011

Calculation Notes

Membrane cost calculation:

Effective area of bipolar membrane = 7.065 cm² (0.0007065 m²)

Area per single anion/cation exchange membrane = 0.0007065 m²

Membrane configuration in the system: 2 bipolar membranes, 1 anion-exchange membrane, and 1 cation-exchange membrane

$$\text{Membrane Cost} = (2 \times P_{\text{bipolar}} + 2 \times P_{\text{single}}) \times 0.0007065$$

where P is the unit price of the corresponding membrane (\$·m⁻²).

Annual Depreciation = Total Investment Cost / Membrane Service Life (3 years)

Annual Fixed Cost = Annual Depreciation + Annual Maintenance Cost
(0.671 \$·year⁻¹)

Unit Fixed Cost = Annual Fixed Cost / Annual Processing Capacity
(1.97 kg·NaOH·year⁻¹)

Sensitivity coefficient:

The sensitivity coefficient is defined as the ratio of the relative change in total cost to the relative change in a given parameter:

$$\text{Sensitivity Coefficient} = \text{Rate of change} / \text{Relative Change in Parameter}$$

When a parameter fluctuates by 20%, the corresponding cost change rate is divided by 0.2 to compute the sensitivity coefficient.

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