Supplementary Information (SI) for Chemical Communications.

Supplementary data for

Regeneration of $LiFePO_4$ from spent lithium-ion battery recycling wastewater via Fenton oxidation-selective precipitation

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This supporting information contains 13-page documents, including 2 Texts, 7 Tables, 3 Figures and this cover page.

Text S1. Synthesis of LFP/C and electrochemical performance testing

A mixture of 20.61 g $Fe_3(PO_4)_2 \cdot 8H_2O$, 5.97 g Li_3PO_4, and 2.0 g $C_6H_{12}O_6$ was combined with 60 mL C_2H_5OH. Subsequently, 0.2 g of phytic acid was added, and the slurry was ground until the particle size was reduced to below 0.5 μm. The resulting slurry was subjected to spray drying and heated at 400 °C for 5.0 h and 800 °C for 8.0 h in an argon-filled square furnace to obtain the LFP/C materials. For comparison, commercial Li_3PO_4 (supplied by a company in Shanghai, China, denoted as C-Li_3PO_4) was also subjected to the same procedure.

The LFP/C material was assembled into CR2025 button batteries and tested at 25 °C. The LFP/C, acetylene black, and PVDF were mixed in a mass ratio of 8:1:1, followed by the addition of an appropriate amount of N-methyl-2-pyrrolidone to form a uniform slurry. The slurry was then evenly coated onto a smooth Al foil, vacuum-dried at 120 °C for 12.0 h, and cut into circular disks with a diameter of 12 mm. The electrolyte was prepared by dissolving ethyl methyl carbonate, ethylene carbonate, and dimethyl carbonate in a 1.0 mol/L solution of $LiPF_6$ at a 1:1:1 volume ratio. Finally, the circular disks, lithium metal counter electrode, and electrolyte were assembled into button batteries in an argon-filled glove box. The electrochemical performance was evaluated using a LAND testing system.

Text S2. Impacts of Na and S impurities in Li_3PO_4 on electrochemical performance

Li_3PO_4 was synthesized using a simulated solution prepared from analytical grade Li_2SO_4 with a Li^+ concentration of 3.0 g/L, following the same synthesis process in this work. The resulting Li_3PO_4 product contained 99.67% Li_3PO_4, with 0.012% Na and 0.003% S. To investigate the impact of Na and S impurities, four Li_3PO_4 samples with varying Na and S contents were prepared by treating the base product with Na_2SO_4 solutions of different concentrations. The total Na and S contents in the samples were as follows: Li_3PO_4@1: 0.015%, Li_3PO_4@2: 0.032%, Li_3PO_4@3: 0.054%, and Li_3PO_4@4: 0.061%. These samples were then used as the precursors to synthesize LFP/C materials, and their initial charge/discharge curves at 0.1C are presented in Fig. R2.

As the Na and S content in Li_3PO_4 increased from 0.015% to 0.061%, the charge/discharge capacity of the corresponding LFP/C materials at 0.1C gradually decreased (from 158.3/157.3 to 151.0/147.8 mAh/g). The initial charge/discharge capacities of Li_3PO_4@1 to Li_3PO_4@4 were as follows: 158.3/157.3, 155.9/154.7, 153.1/150.7, 151.0/147.8 mAh/g. Therefore, the electrochemical performance of the regenerated LFP/C material was found to be primarily influenced by Na and S impurities, rather than by the crystal structure of Li_3PO_4. The acceptable initial charge/discharge capacity in the Standard (YS/T 1027-2024) is 153 mAh/g, suggesting that the threshold for Na/S impurity content in Li_3PO_4 product is 0.054%. Our regenerated R-Li_3PO_4 from wastewater (with Na/S impurity content of 0.042% and capacity of 153.4 mAh/g at 0.1 C) falls within this scope.

Table S1. Elemental compositions of the wastewater used in this work. /mg·L^{-1}

Composition	Li	Ni	Mn	S	Na	Ca	Mg	P	oil
Wastewater	2733	4.8	151	21700	28690	18.2	15.3	70.8	232

Note: Elemental concentrations were quantified using inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer, Avio 200), and oil content was determined with an infrared spectrophotometric oil analyzer (ZFO-1100, China). Its composition includes residual elements from the selective recovery of Ni, Co, Mn, and Li. S originates from the leaching agents used, while Na is introduced through the addition of Na_2CO_3 during the recovery of Li_2CO_3. Cu and Al are derived from the current collectors of the battery anode and cathode, respectively. Mg is typically added as a dopant in cathode materials to enhance battery performance. Ca may originate from battery sealants, binders, or ceramic separators, and may also be related to the hardness of the process water. Fe is introduced during the Cu replacement process, while P and oily pollutants are introduced from the extractants used in the recovery process.

Table S2. Chemical reactions involved in the Fenton-Flocculation precipitation process.

No.	Chemical reactions
1	$Fe(II) + H_2O_2 \rightleftharpoons Fe(III) + \cdot OH + OH^-$
2	$Fe(III) + H_2O_2 \rightleftharpoons Fe(II) + \cdot HO_2 + H^+$
3	$Fe(II) + \cdot OH \rightleftharpoons Fe(III) + OH^-$
4	$Fe(III) + \cdot OH \rightleftharpoons Fe(II) + H^+ + O_2\uparrow$
5	$H_2O_2 + \cdot OH \rightleftharpoons H_2O + \cdot HO_2$
6	$R - O - PO_3H_2 + \cdot OH \rightleftharpoons Degradation\ products + H_2O$
7	$Fe^{3+} + 3HA_{(org)} \rightleftharpoons FeA_{3(org)}\downarrow + 3H^+$
8	$Ca^{2+} + 2OH^- = Ca(OH)_2\downarrow$
9	$Ca^{2+} + SO^{2-}_4 = CaSO_4\downarrow$
10	$Mg^{2+} + 2OH^- = Mg(OH)_2\downarrow$
11	$Mn^{2+} + 2OH^- = Mn(OH)_2\downarrow$
12	$Ni^{2+} + 2OH^- = Ni(OH)_2\downarrow$
13	$Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow$

Table S3. Industrial-scale application validation of oily pollutants removal process.

No.	treatment capacity /m^3	oil content /mg/L	*$FeSO_4$ dosage /kg	#H_2O_2 dosage /L	oil in purified liquid /mg/L	oil removal efficiency /%
1#	41.0	106.0	304	225	1.69	98.39
2#	40.5	93.0	263	195	2.28	97.53

*$FeSO_4$ is of industrial grade, with an Fe^{2+} content of 18.5%;

#H_2O_2 is of industrial grade, with a concentration of 27.5% by mass.

Table S4. The composition of the Li_3PO_4 products. /%

No.	Li_3PO_4	Ca	Mg	Ni	Al	Fe	Na	S
C-Li_3PO_4	99.38	0.002	0.016	0.0003	ND	0.0002	0.029	0.001
R- Li_3PO_4	99.51	0.0015	0.003	ND	ND	0.0005	0.033	0.009
r- Li_3PO_4	97.75	0.059	0.041	0.016	0.009	0.012	0.635	0.379

Note: Elemental concentrations were quantified using ICP-OES (PerkinElmer, Avio 200).

Table S5. Economic assessment for the regeneration of 81.5 m^3 of LIBs recycling wastewater using the approach described in this work.

Wastewater oily pollutants removal process				
classification	designation	quantity	unit price	expenditure /$
equipment	reaction tank	12.0 h	0.42 $/h	-5.04
	filter press	6.0 h	0.39 $/h	-2.34
chemicals	$FeSO_4$	0.57 t	42.55 $/t	-24.25
	H_2O_2	0.42 m^3	156.03 $/m^3	-65.53
	H_2SO_4	0.16 m^3	49.65 $/m^3	-7.94
	NaOH	0.40 m^3	150.35 $/m^3	-60.14
energy consumption	electrical energy	12.0 h	1.70 $/h	-20.40
	labor cost	12.0 h*2	2.0 $/h	-48.0
others	waste management	0.30 t	283 $/t	-84.9
Total sub cost:			**-3.91 $/m^3**	

Li_3PO_4 products recovery process				
classification	designation	quantity	unit price	expenditure $
equipment	reaction tank	7.0 h	0.42 $/h	-2.94
	filter press	10.0 h	0.39 $/h	-3.9
	ball mill	2.0 h	0.20 $/h	-0.40
	roasting furnace	10.0 h	1.18 $/h	-11.80
chemicals	$Na_3PO_4 \cdot 12H_2O$	3.8 t	453.9 $/t	-1724.82
	H_2O	8.0 m^3	0.26 $/m^3	-2.08
energy consumption	electrical energy	/	/	-205.95
	steam	1.5 m^3	32.62 $/t	-48.93
	labor cost	12 h*2	2.0 $/h	-48.0
products	Li_3PO_4	0.92 t	7940 $/t	+7304.8
Total sub cost:			**+64.49 $/m^3**	

Table S6. Economic assessment for treating 81.5 m^3 of wastewater by adsorption.

classification	**designation**	**quantity**	**unit price**	**expenditure /$**
equipment	reaction tank	6.0 h	0.42 $/h	-2.52
	filter press	3.0 h	0.39 $/h	-1.17
chemicals	activated carbon	0.125 t	1585 $/t	-198.13
	H_2SO_4	0.10 m^3	49.65 $/m^3	-5.0
energy consumption	electrical energy	6.0 h	1.70 $/h	-10.2
	labor cost	12.0 h*2	2.0 $/h	-48.0
others	waste management	0.21 t	283 $/t	-59.43
Total sub cost:			**-3.98 $/m^3**	

Table S7. The composition of the filtrate after Li_3PO_4 recovery. /mg/L

Composition	Li	Ca	Mg	Mn	P	Ni	Na	S	oily pollutants
Filtrate	150	0.2	0.7	ND	580	ND	33960	25100	0.56

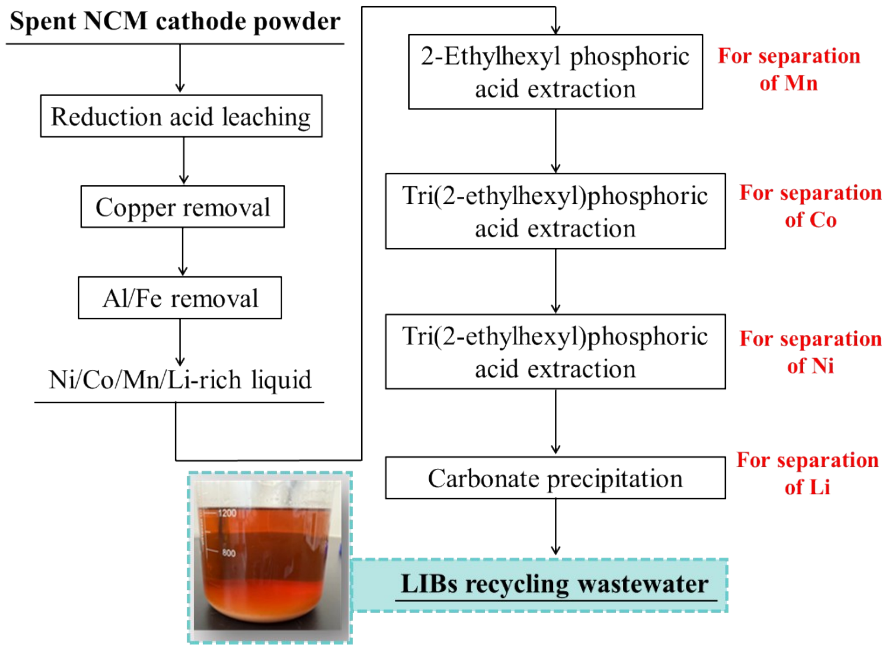

Fig. S1. The generation process of the wastewater used in this work.

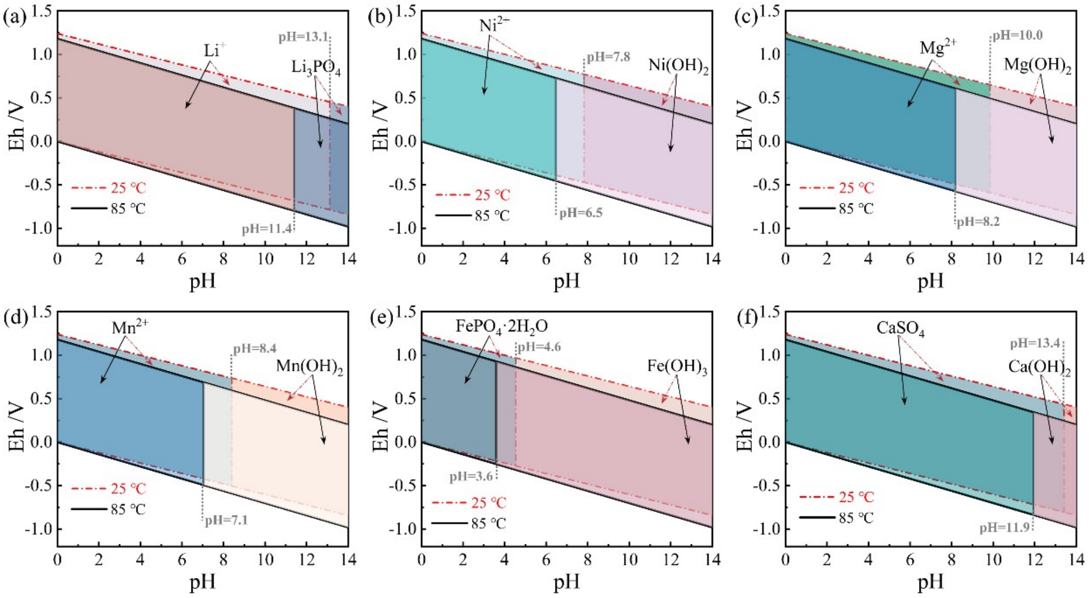

Fig. S2. Eh-pH diagram for the Li-Ni-Mg-Mn-Fe-Ca-P-Na- SO_4^{2-}-H_2O system at 25 ^{o}C and 85 ^{o}C ([Li]=[P]=0.5 mol/L, [Mn]=0.01 mol/L, [Ni]=[Mg]=[Fe]=[Ca]=0.001 mol/L, [Na]=[S]=1.0 mol/L).

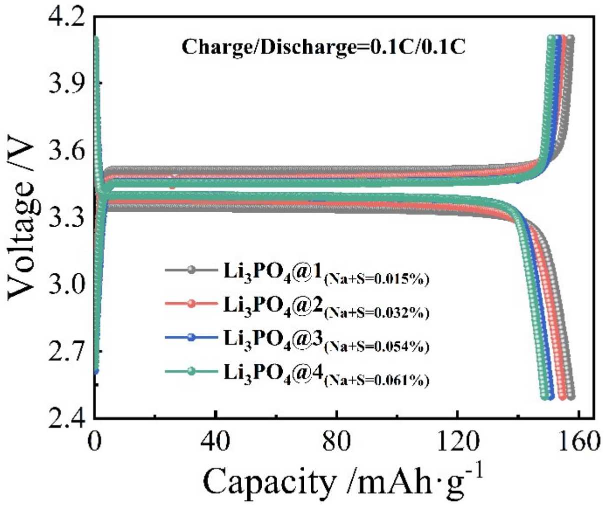

Fig. S3. Initial charge/discharge capacity of LFP/C batteries at 0.1C generated from the synthesized Li_3PO_4 with varying Na/S impurity content.