Supporting Information for

Recycling of spent $LiFePO_4$ batteries with acid-free process to high-rate $Na_2FeP_2O_7$@C cathodes for sodium-ion storage

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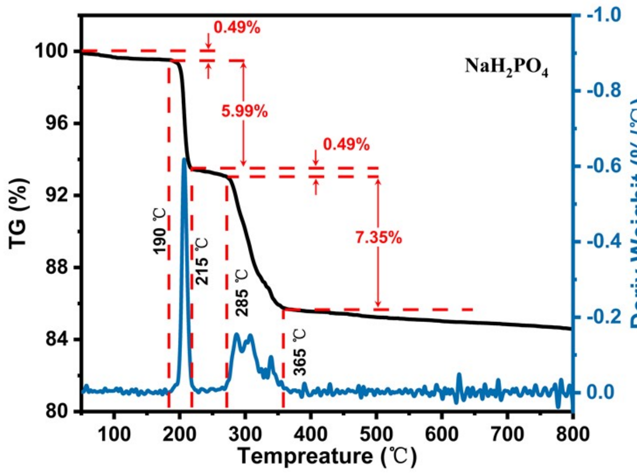

Fig. S1. TGA-Derived Mass Loss Characteristics of NaH_2PO_4 During Pyrolysis

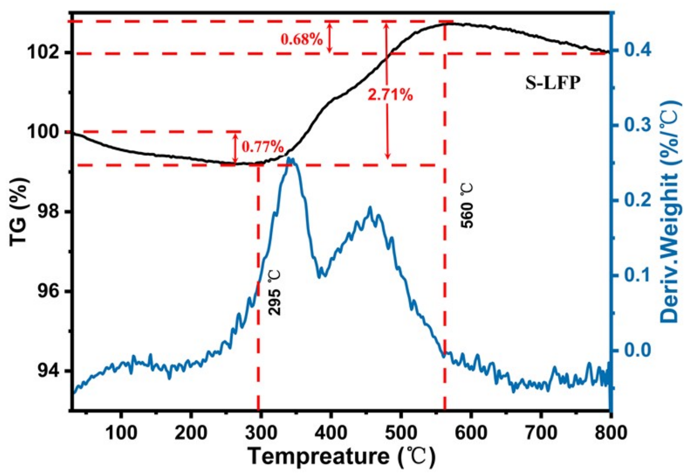

Fig. S2. TGA-Derived Mass Loss Characteristics of S-LFP During Pyrolysis

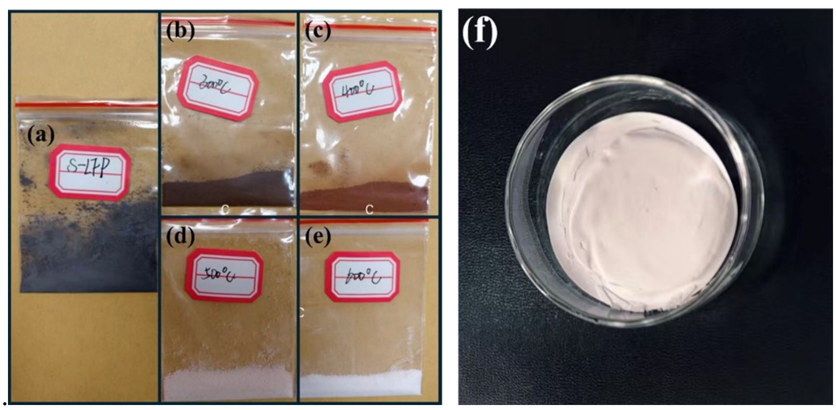

Fig. S3. Digital photographs of (a) spent LFP cathode powder, (b-e) roasted powders at different calcination temperatures, and (f) the dried leaching residue.

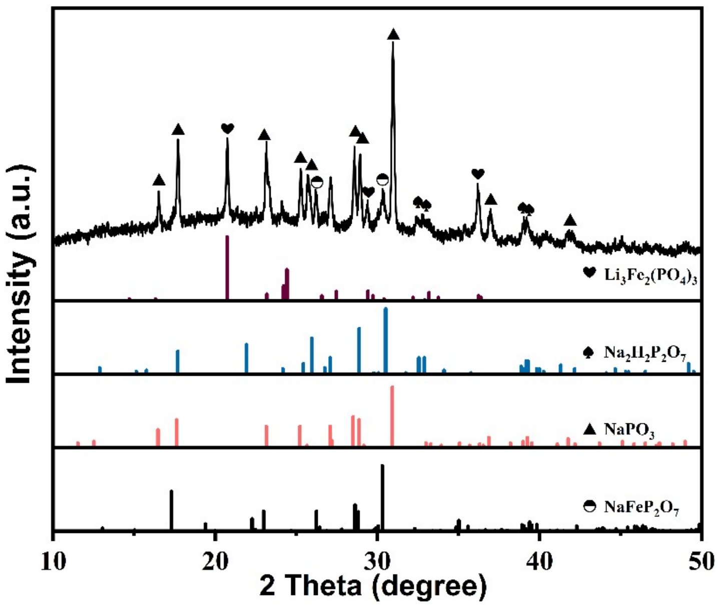

Fig. S4. XRD pattern of the S-LFP/NaH_2PO_4 mixture roasted at 600 °C for 10 min.

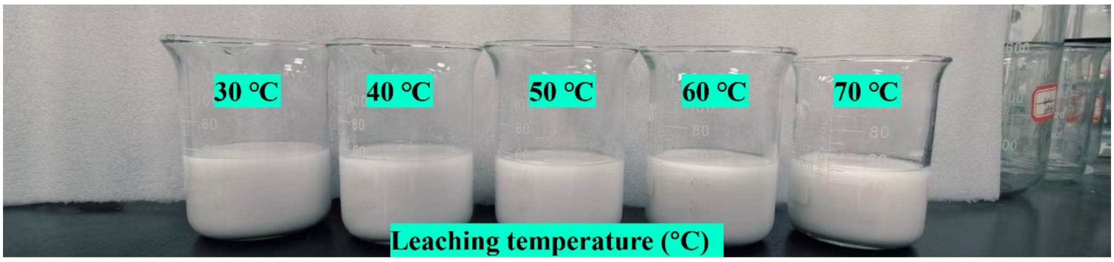

Fig. S5. Digital photographs of leaching slurries under different leaching temperatures (30-70 °C).

Fig. S6. Digital photographs of leaching slurries under different solid-to-liquid ratios (10-250 g·L^{-1})

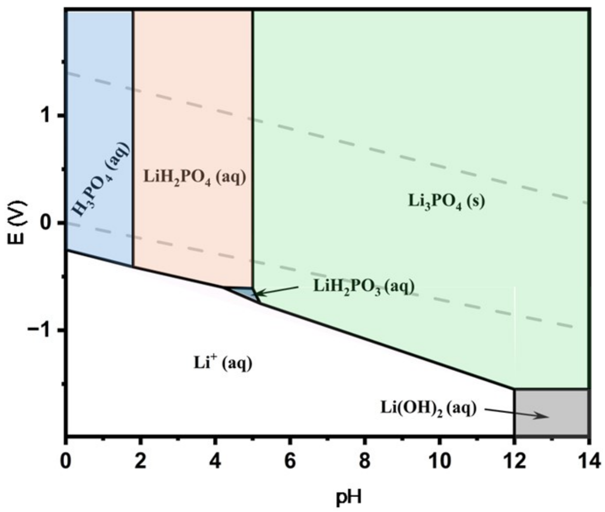

Fig. S7. The E-pH diagram of the Li-Fe-P-H_2O system at 298.15 K.

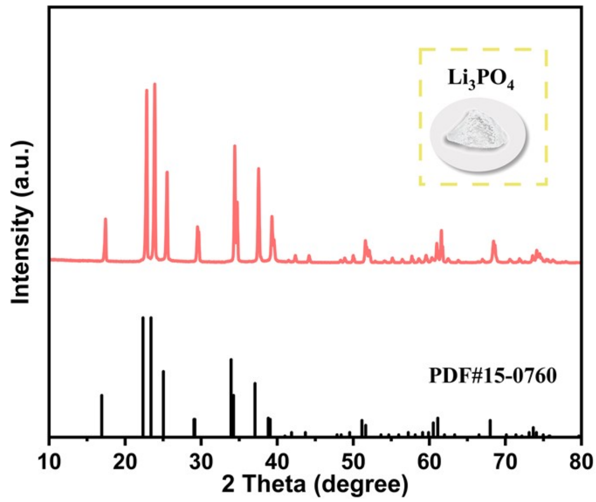

Fig. S8. XRD pattern of Li_3PO_4.

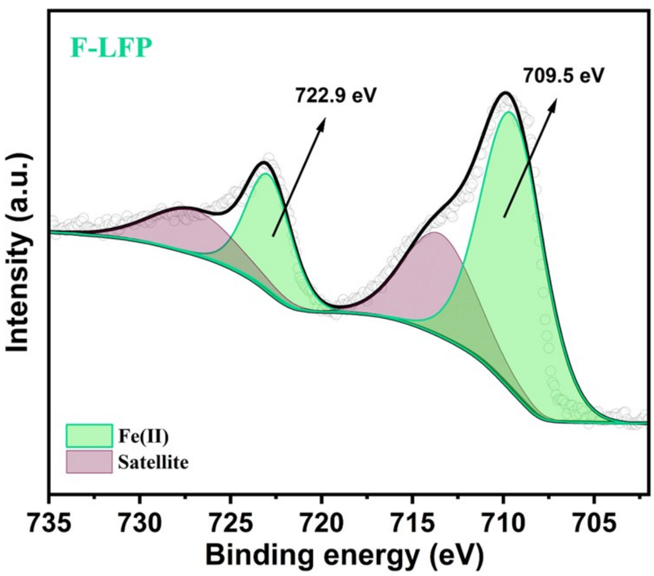

Fig. S9. Fe 2p XPS spectrum of the F-LFP powder.

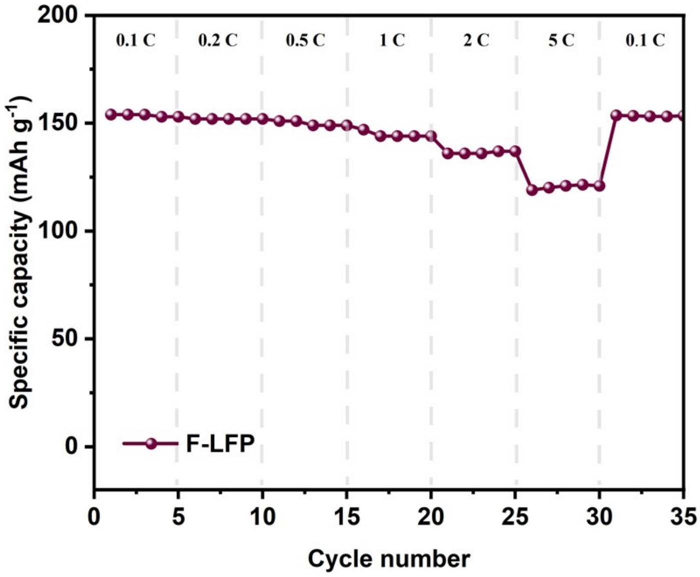

Fig. S10. Rate capability of F-LFP under varying C-rates.

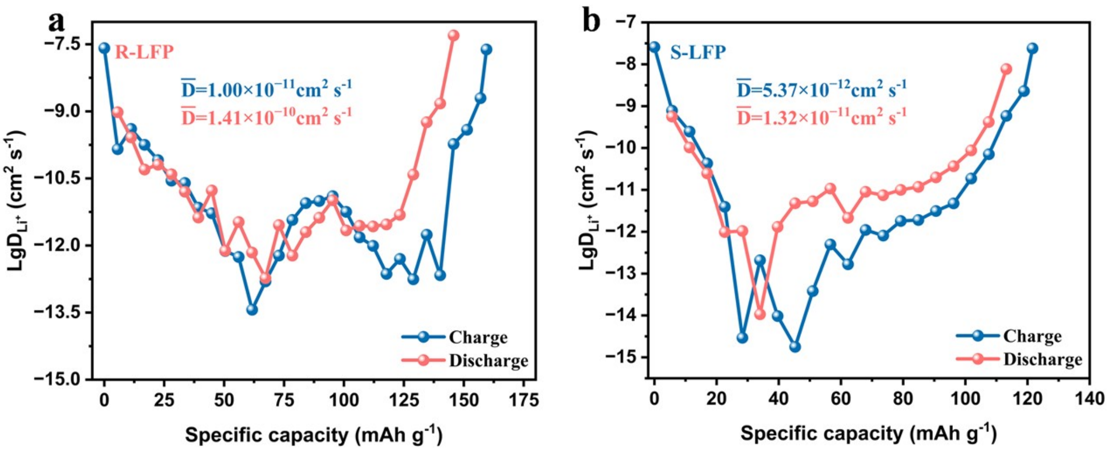

Fig. S11. (a, b) corresponding Li^+ ion diffusion coefficient of R-LFP and S-LFP electrode.

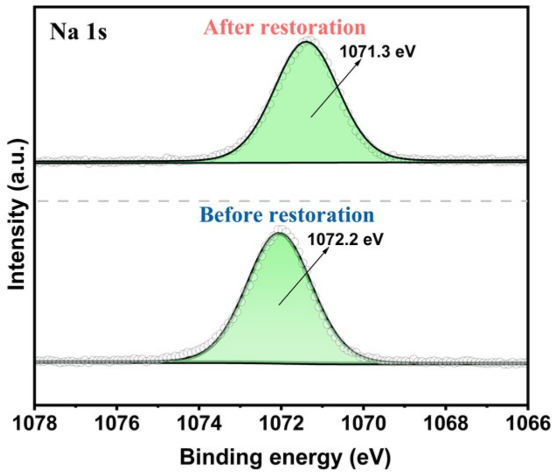

Fig. S12. High-resolution XPS spectra of the Na 1s level before and after reduction.

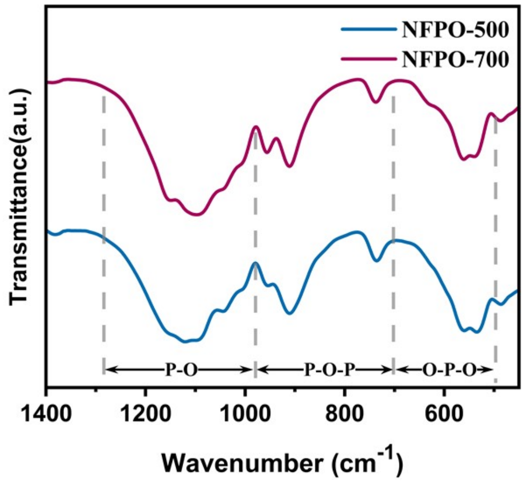

Fig. S13. FTIR spectra of NFP-500, and NFP-700.

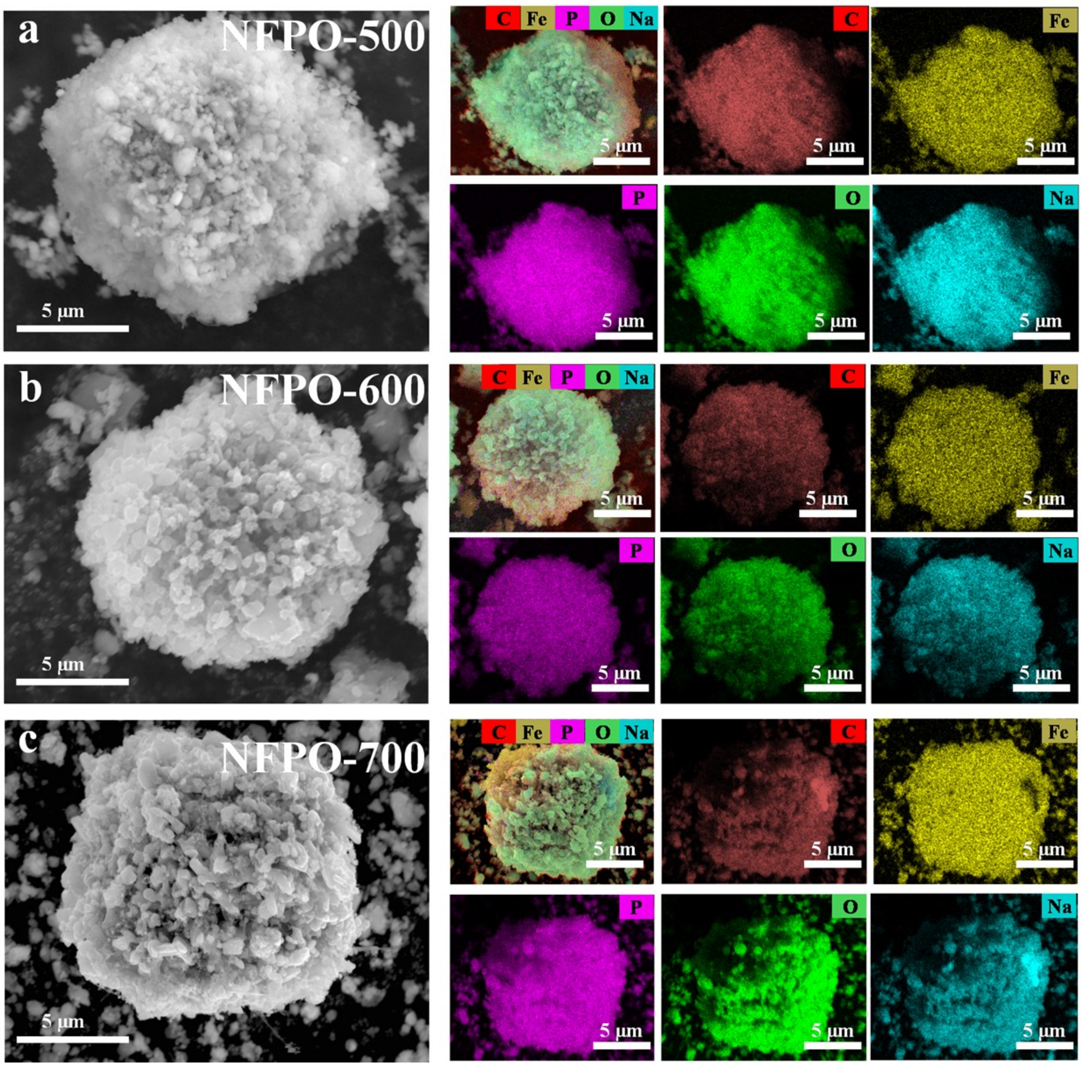

Fig. S14. (a-c) STEM-EDS elemental mapping images of Na, Fe, P, O and C for NFPO-500, NFPO-600 and NFPO-700.

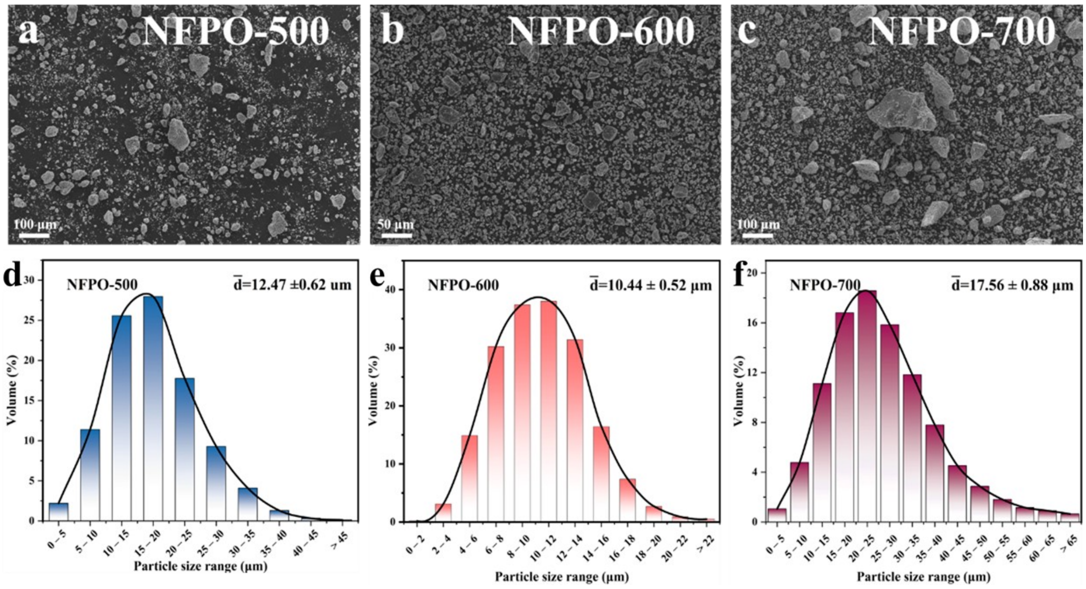

Fig. S15. (a-c) High-magnification SEM images and (d-f) particle size distributions of NFPO-500, NFPO-600, and NFPO-700.

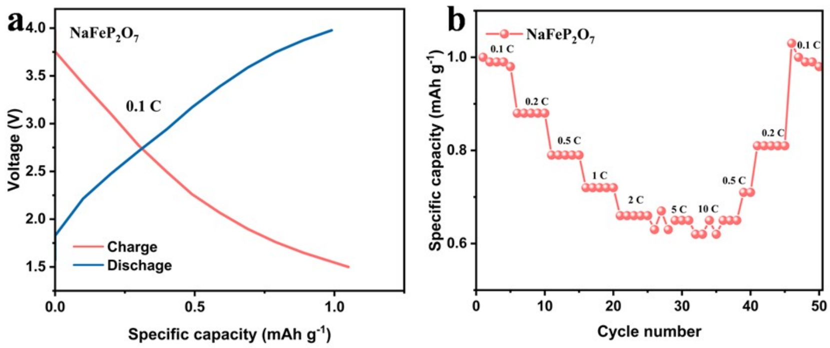

Fig. S16. (a) Charge and discharge curves of $NaFeP_2O_7$ at 0.1 C, (B) Rate capability NFPO-HC at different current rates.

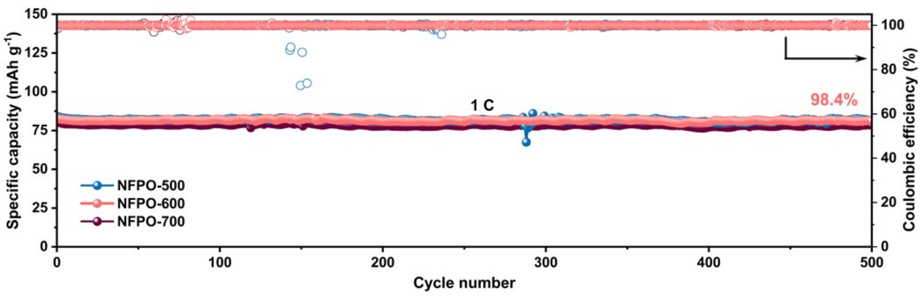

Fig. S17. Cycling performance of NFPO-500, NFPO-600, and NFPO-700 at 1 C.

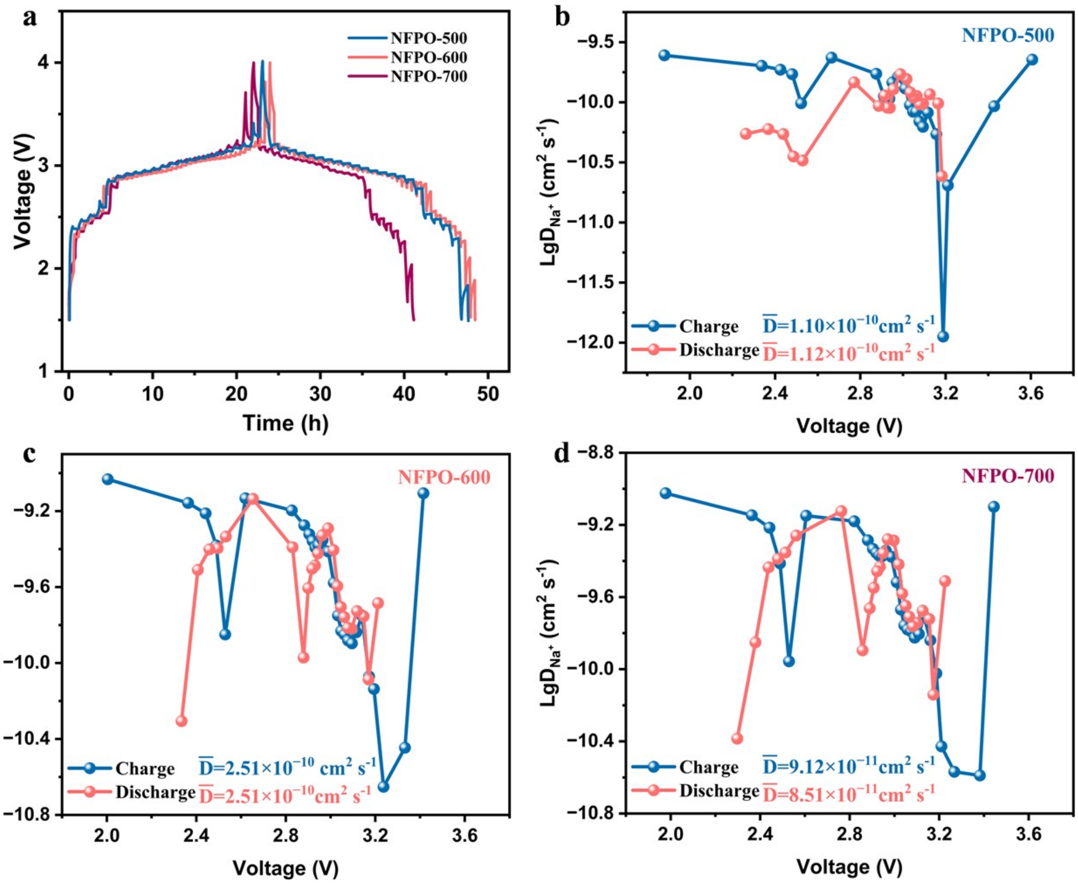

Fig. S18. (a) GITT curves of NFPO-500, NFPO-600 and NFPO-700 electrodes. (b, c, d) Corresponding Na^+ ion diffusion coefficients of NFPO-500, NFPO-600 and NFPO-700 electrodes during charge-discharge processes.

$$D_K = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_L}\right)^2\left(\tau = \frac{L^2}{D}\right) \qquad \text{(Equation S1)}$$

Where τ refers to constant current pulse time, m_B, V_M, M_B, and S are the mass, molar volume, molar mass, and electrode-electrolyte interface area, respectively. ΔE_S is the voltage difference of one pulse-relaxation period, and ΔE_τ is the voltage difference of one constant current pulse.[1]

Where τ is the constant current pulse time, m_B, M_B, and S are the mass, molar mass, and electrode-electrolyte interface area of the active material, respectively. ΔE_S is the steady-state voltage change during the pulse, and ΔE_τ is the voltage change during the constant current pulse. The key parameter molar volume (V_M) is defined as the volume occupied by one mole of a substance and is calculated by:

$$V_M = M_B / \rho \qquad \text{(Equation S2)}$$

where ρ is the theoretical density of the material, derived from its crystal structure. The molar volumes for the specific materials discussed were calculated as follows:

For $LiFePO_4$ (R-LFP and S-LFP in Fig. S5):

Molar Volume (V_M): $V_M = M_B/\rho$ = 157.76 g/mol / 3.6 g/cm³ = 43.82 cm³/mol

For $Na_2FeP_2O_7$ (NFPO electrodes in Fig. S8):

Molar Volume (V_M): $V_M = M_B/\rho$ = 274.75 g/mol / 3.25 g/cm³ = 84.54 cm³/mol

These calculated V_M values were then used in Equation S1 to determine the Li^+ and Na^+ ion diffusion coefficients presented in Figs S5 and S8.

Table S1. Elements composition of cathode scrap

Elements	Fe	Li	Al	P	C
wt%	35.47	4.07	0.16	18.29	4.38

Table S2. Enthalpy changes of main reactions obtained by linear fitting of ΔG−T curves

No.	Reaction equation	Enthalpy change ΔH ($kJ\cdot mol^{-1}$)·
1	$2NaH_2PO_4=Na_2H_2P_2O_7+H_2O(g)$	79.98
2	$Na_2H_2P_2O_7=2NaPO_3+H_2O(g)$	100.11
3	$2FePO_4+Na_2H_2P_2O_7=2NaFeP_2O_7+H_2O(g)$	114.63
4	$Li_3PO_4+5Na_3PO_4=3LiNa_5(PO_4)_2$	-23.79
5	$Fe_2O_3+P_2O_5(g)=2FePO_4$	-275.66
6	$Li_3Fe_2(PO_4)_3=Li_3PO_4+Fe_2O_3+P_2O_5(g)$	-253.15
7	$3NaPO_3=Na_3PO_4+P_2O_5(g)$	-185.66
8	$LiFePO_4+1/4O_2(g)=1/3Li_3Fe_2(PO_4)_3+1/6Fe_2O_3$	-54.20
9	$Li_3PO_4+6NaPO_3=Li2NaPO_4+LiNa_5(PO_4)_2+2P_2O_5(g)$	109.99

Table S3. Elements composition of recycled Li_3PO_4

Elements	Li_3PO_4	Fe	Al	Na
wt%	99.65%	0.008%	0.005%	0.085%

Table S4. Resource inputs required to recycle 1 t of S-LFP batteries via Pyrometallurgy

Pyr. (Pyrometallurgy)			
Consumption	Price (\$/t)	Dosage (t)	Cost (\$)
S-LFP	1376.87	1	1376.87
Coke	559.66	0.18	100.74
$CaCO_3$	27.93	0.15	4.19

Na_2CO_3	275.37	0.0837	23.05
NaOH	384.07	2.0538×10^{-4}	0.10
Water	0.46	20	9.20
Electricity	0.11	2450	269.50
Wastewater	8.23	20	164.60
Maintenance fee	/	41.4137	230.40
Labor cost	/	/	349.44
Other expenses	/	/	170.41
Total ($)		2698.50	

Note: 1 $ = 7.18 ￥ (Update time: 2025/9)

The "Other expenses" item encompasses typical operational overhead inherent to industrial-scale production, primarily comprising energy consumption, costs of precursor materials and chemicals, as well as expenses associated with reagent recycling and processing.

Table S5. Resource inputs required to recycle 1 t of S-LFP batteries via Hydrometallurgy

Hyd. (Hydrometallurgy)			
Consumption	Price ($/t)	Dosage (t)	Cost ($)
S-LFP	1376.87	1	1376.87
H_2SO_4	1080.25	0.089	96.14
H_2O_2	115.94	0.112	12.99
Na_3PO_4	907.82	0.268	243.30
NaOH	384.07	5.1345×10^{-4}	0.20
Water	0.46	50	230.00
Electricity	0.11	300	33.00
Wastewater	18.23	50	911.50
Maintenance fee	/	/	767.60
Labor cost	/	/	363.12
Other expenses	/	/	170.41
Total ($)		4205.13	

Note: 1 $ = 7.12 ￥ (Update time: 2025/9)

The "Other expenses" item encompasses typical operational overhead inherent to industrial-scale production, primarily comprising energy consumption, costs of precursor materials and chemicals, as well as expenses associated with reagent recycling and processing.

Table S6. Resource inputs required to recycle 1 t of S-LFP batteries via Auxiliary roasting

Auxiliary roasting (AR)			
Consumption	Price ($/t)	Dosage (t)	Cost ($)
S-LFP	1376.87	1	1376.87
NaH_2PO_4	677.37	2.5	1693.43
$FePO_4$	642.45	0.925	594.27
CH_3COONa	345.02	0.520	179.41
Sucrose	812.85	0.338	274.743
Na_3PO_4	302.61	0.268	80.80
NaOH	384.07	3.0538×10^{-4}	0.11

Water	0.36	30	10.80
Electricity	0.11	500	55.00
Wastewater	8.23	3	24.69
Maintenance fee	/	535.682	52.30
Labor cost	/	/	432.45
Other expenses	/	/	170.41
Total ($)		4945.28	

Note: 1 $ = 7.12 ￥ (Update time: 2025/9)

The "Other expenses" item encompasses typical operational overhead inherent to industrial-scale production, primarily comprising energy consumption, costs of precursor materials and chemicals, as well as expenses associated with reagent recycling and processing.

Table S7. Economic Benefits of Recycling 1 t of S-LFP Batteries via Pyrometallurgy Process

Pyr. (Pyrometallurgy)			
Product	Price ($/t)	Dosage (t)	Revenue ($)
Li_2CO_3	13268.16	0.17	2255.59
Phosphorus iron slag	167.59	0.48	80.44
Total ($)		2336.03	
Profit		-362.47	

Note: 1 $ = 7.12 ￥ (Update time: 2025/9)

Table S8. Economic Benefits of Recycling 1 t of S-LFP Batteries via Hydrometallurgical Process

Hyd. (Hydrometallurgy)			
Product	Price ($/t)	Dosage (t)	Revenue ($)
Li_3PO_4	33334.78	0.13	4333.52
$FePO_4$	1942.11	0.956	1864.43
Total ($)		6197.95	
Profit		1,992.82	

Note: 1 $ = 7.12 ￥ (Update time: 2025/9)

Table S9. Economic Benefits of Recycling 1 t of S-LFP Batteries via Auxiliary roasting Process

Auxiliary roasting (AR)			
Product	Price ($/t)	Dosage (t)	Revenue ($)
R-LFP	2935.113	0.967	2847.06
NFPO	3522.134	1.413	4966.20
Total ($)		7813.26	
Profit		2867.98	

Note: 1 $ = 7.12 ￥ (Update time: 2025/9)

Table S10. Calculation of the E-factor for the assisted roasting (AR) process based on treating 1 kg of S-LFP scrap

Parameter	Value / Description
Total input	1 kg S-LFP + 2.5 kg NaH_2PO_4 + 0.925 kg $FePO_4$ + 0.52 kg CH_3COONa +

materials	0.338 kg sucrose = 5.283 kg
Target product mass	0.967 kg R-LFP + 1.413 kg NFPO = 2.38 kg
Waste mass (estimated)	Mainly washing water and roasting off-gas, actual discharged waste ≈ 0.5 kg
E-factor	Waste mass / Product mass = 0.5 / 2.38 ≈ 0.21
Significance	Far lower than conventional hydrometallurgy (E-factor > 20) and pyrometallurgy (E-factor > 10), indicating high atom economy and minimal waste emission.

Note: E-factor is defined as the ratio of total waste mass to target product mass, serving as a measure of the "cleanness" of a process.

Table S11. P/Na closed-loop mass balance for the treatment of 1 tonne of S-LFP scrap

Stream	P mass (kg)	Na mass (kg)	Remarks and data source
S-LFP scrap	182.9	0	Table S2: P 18.29 wt%
Fresh NaH_2PO_4 (first use)	645.0	479.0	Table S5: 2.5 t, P 25.8%, Na 19.16%
Entering NFPO product	317.4	235.7	Table S8: 1.413 t, P 22.46%, Na 16.68%
Entering R-LFP product	0	0	Uses purchased $FePO_4$; no P/Na consumed from the system
Loss in wastewater	8.3	20.0	based on consideration of solution residue and washing efficiency
Recovered by off-gas absorption system (for NaH_2PO_4 regeneration)	502.2	223.3	Residual amount (479.0 – 235.7 – 20.0 = 223.3)
Net make-up after circulation	0	149.3	Requires NaOH addition to achieve a Na/P molar ratio of 1:1 (required for NaH_2PO_4)
Closed-loop efficiency	P recovery 99.0%	Na recovery 95.8%	(Input – Loss) / Input; Na input = 479.0 kg

Note: The net Na make-up is calculated as follows: in the recovered stream, Na = 223.3 kg, P = 502.2 kg, giving a Na/P molar ratio of (223.3/23) / (502.2/31) = 9.71 / 16.20 = 0.60. To adjust this ratio to 1:1, the required additional amount of Na is 16.20 – 9.71 = 6.49 kmol, corresponding to a Na mass of 6.49 × 23 = 149.3 kg.

Table S12. Comparison of greenhouse gas emissions for different recycling processes treating 1 tonne of S-LFP scrap

Process	Relative GHG emission level	Main sources
Pyrometallurgy (Pyro)	Very high	High-temperature roasting (>1200 °C), coke combustion
Hydrometallurgy	High	Acid/alkali production, energy consumption for

(Hydro)		wastewater treatment
$K_2S_2O_7$-based full regeneration	Low	Roasting at 600 °C, but $K_2S_2O_7$ cannot be recycled [2]
This work (AR)	Low	Roasting at 600 °C + carbothermal reduction at 700 °C, partial reagent closure

References

[1] Y.-J.Wang, Z.-Y.Gu, D.-S.Bai, Z.-L.Hao, H.-W.Huang, Y.Yan, C.-J.Li, A.-M.Liu, X.-L.Wu, Angew. Chem. Int. Ed. 2025, e202507573.

[2] H. Hu, X. Meng, Y. Li, Y. Yang, Y. Xu, J. Hu, Y. Yao, ACS Sustainable Chem. Eng. 12 (2024) 16553-16563.