Supplementary Information

Driving the rapid regeneration of $LiFePO_4$ from spent lithium-ion batteries through one-pot mechanochemical activation

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This file includes Figures. S1 to S11, Tables S1 to S5 and Texts S1 to S2.

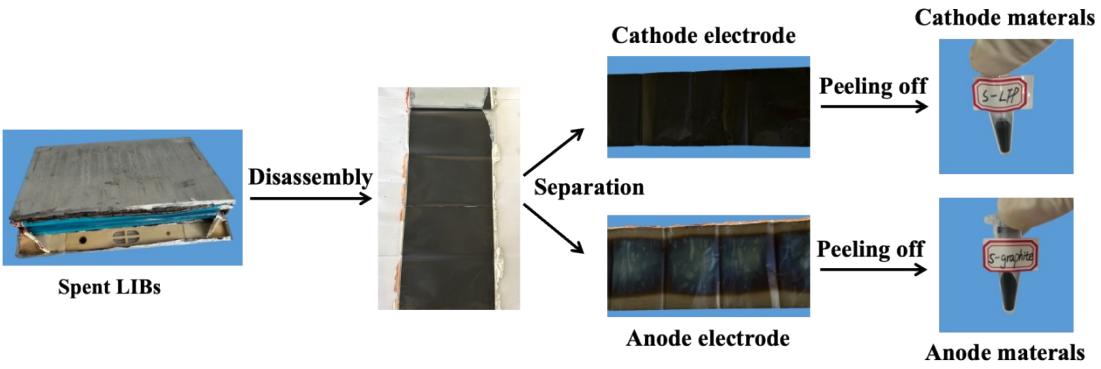

Fig. S1. Recycling procedure of spent LIBs.

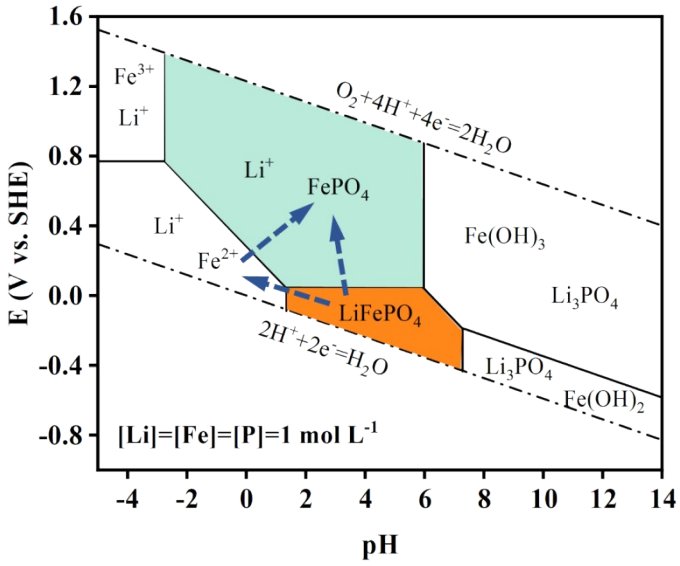

Fig. S2. E-pH diagram of the Li–Fe–P-H_2O system and the relationship between the electrode potential of redox couples and pH (25 °C).

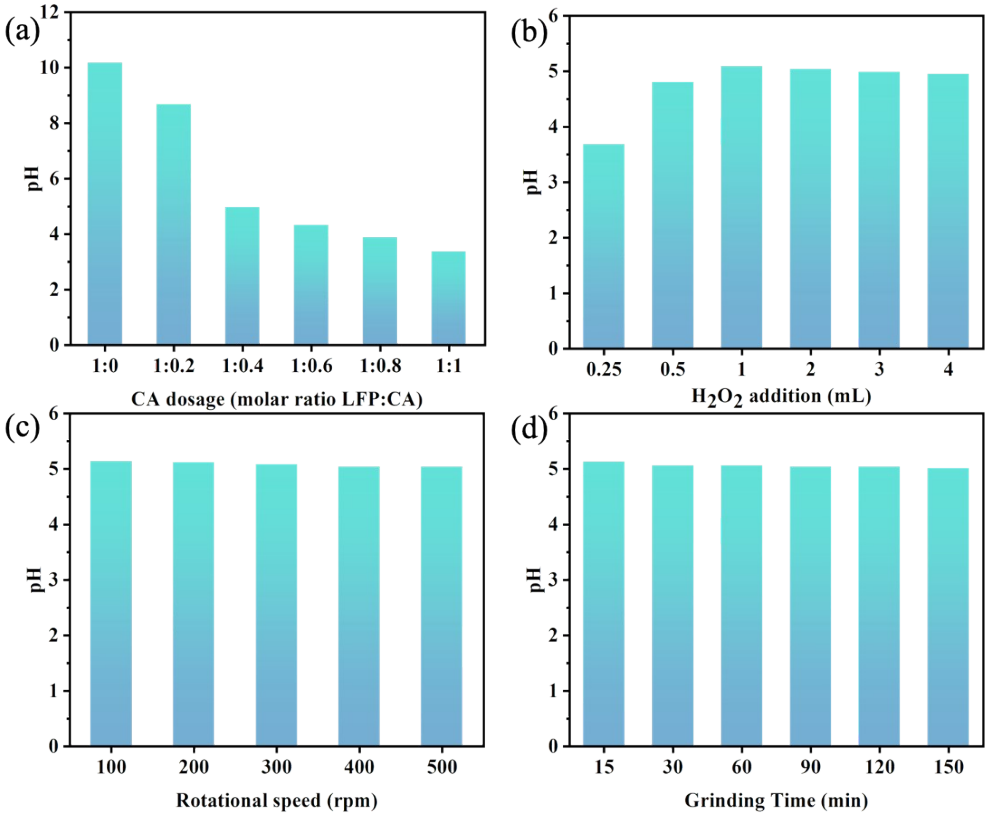

Fig. S3. pH of leaching solutions under different leaching conditions.

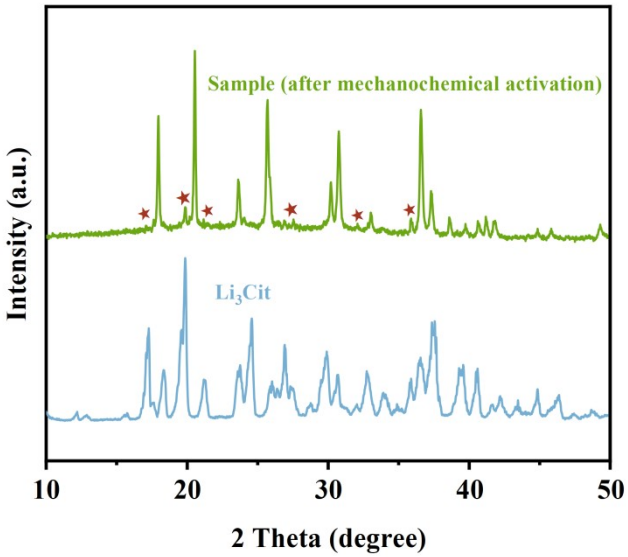

Fig. S4. XRD pattern of sample (directly-dried LFP after mechanochemical activation).

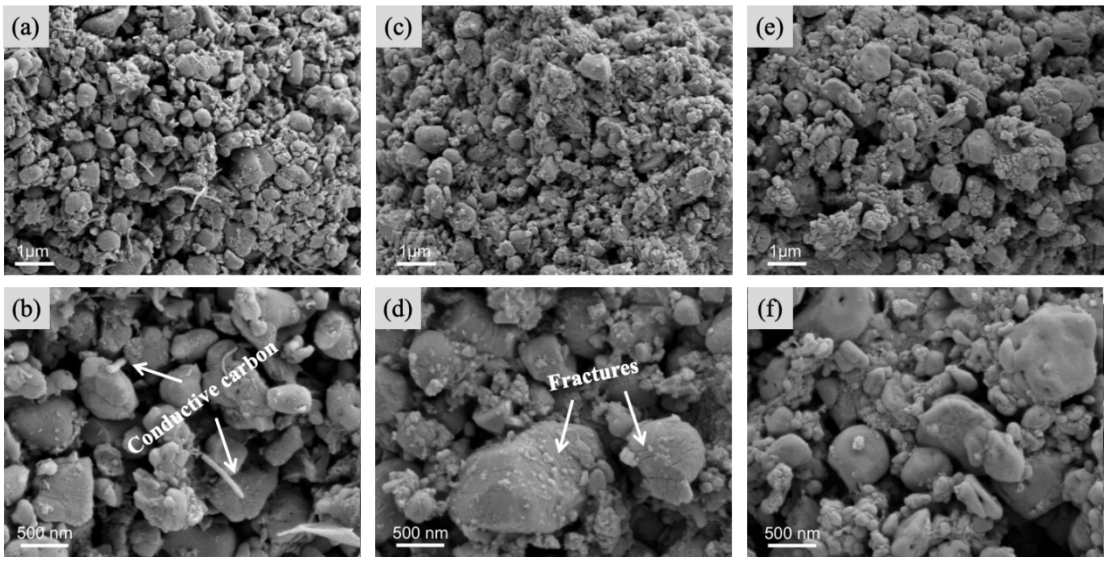

Fig. S5. SEM images of different samples at low and high resolutions. (a, b) S-LFP, (c, d) precursors, (e, f) R-LFP.

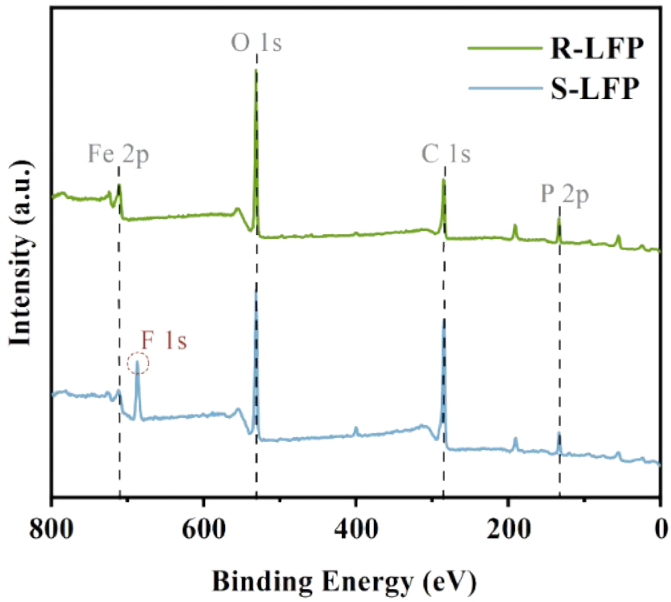

Fig. S6. XPS survey of S-LFP and R-LFP.

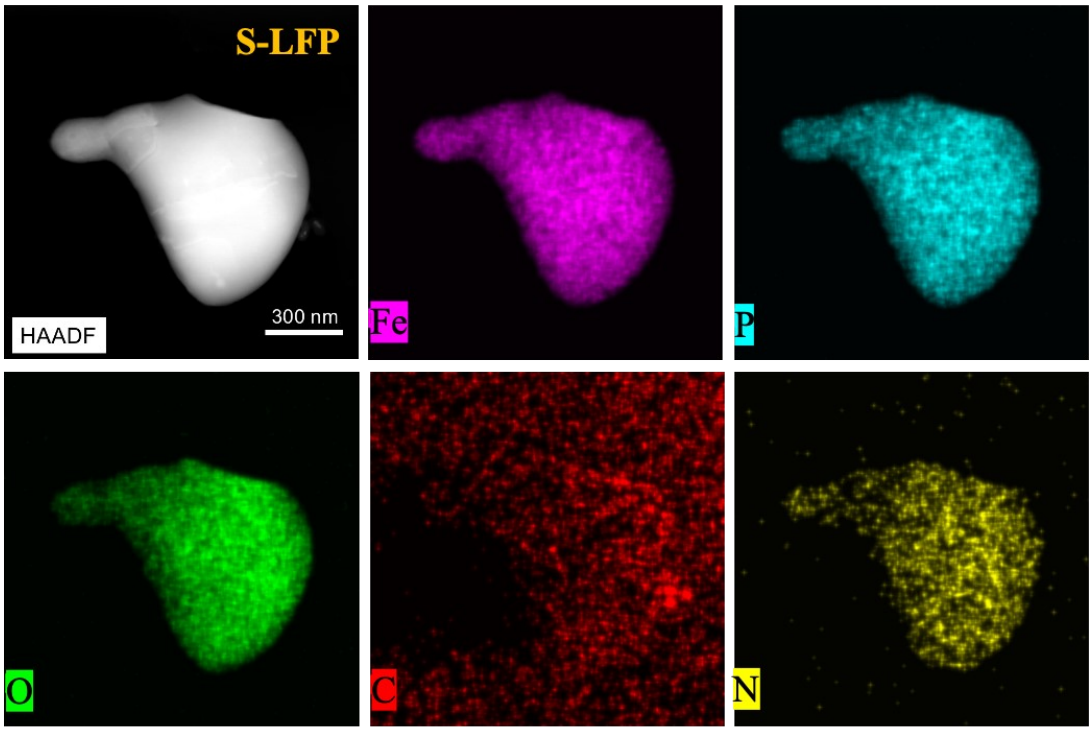

Fig. S7. EDS elemental maps of S-LFP.

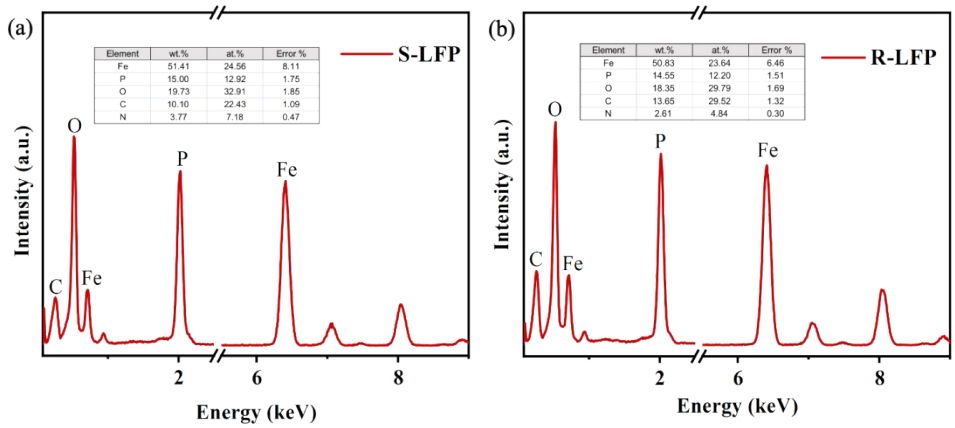

Fig. S8. EDS energy spectra of (a) S-LFP and (b) R-LFP.

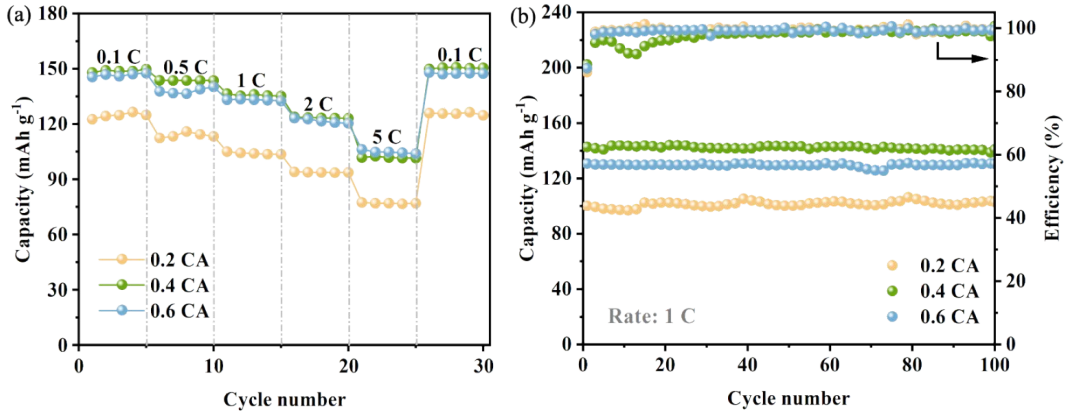

Fig. S9. The (a) rate capability and (b) cycling performance of R-LFP obtained at different CA additions.

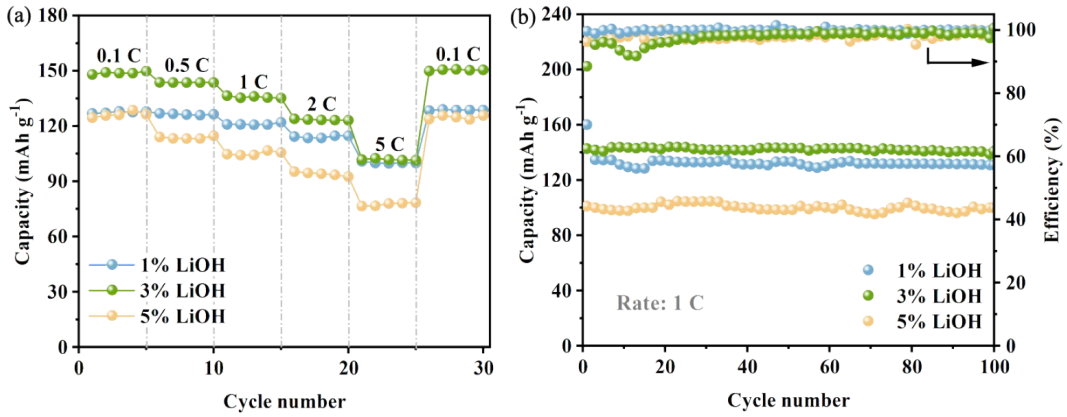

Fig. S10. The (a) rate capability and (b) cycling performance of R-LFP obtained at different LiOH additions.

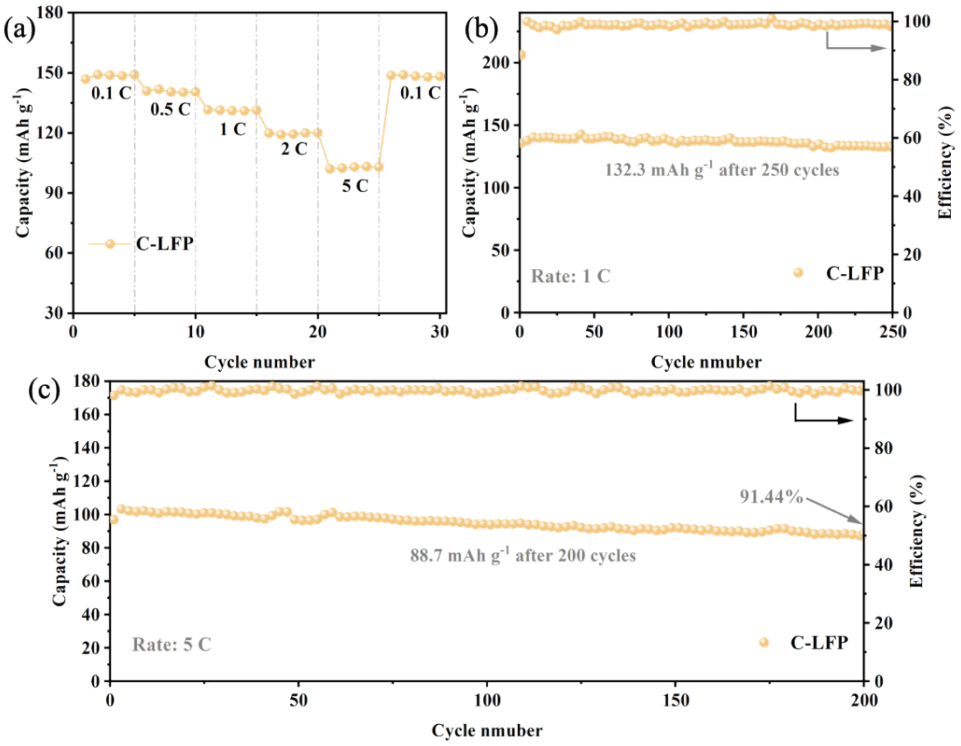

Fig. S11. The (a) rate capability of C-LFP. The long-term cycling capability of C-LFP at (b) 1 C for 250 cycles and (c) 5 C for 200 cycles.

Table S1. ICP-OES analysis of the solution from S-LFP and R-LFP.

S-LFP	Fe (mol):P (mol): Li (mol)	1:0.96:0.92
R-LFP		1:0.98:1.03

Table S2. Structural parameters obtained from Rietveld refinement of the XRD pattern of S-LFP. **Phase 1 $LiFePO_4$:** Space group: *Pnma*, a=10.314343 Å, b=5.999137 Å, c=4.688912 Å, α=β=γ=90°. **Phase 2 $FePO_4$:** Space group: *Pnma*, a=9.836868 Å, b=5.800138 Å, c=4.785726 Å, α=β=γ=90°.

	81.44% $LiFePO_4$					**18.56% $FePO_4$**			
Atoms	**Site**	**Wyckoff positions**			**Occupancy**	**Site**	**Wyckoff positions**		**Occupancy**
Li	4a	0	0	0	0.94000	NA			
Fe	4a	0	0	0	0.06000	4a	0.00000	0.00000	0.00000	0.00200
Fe	4c	0.28191	0.25000	0.97418	0.94000	4c	0.28396	0.25000	0.96998	0.99800
Li	4c	0.28191	0.25000	0.97418	0.06000	NA			
P	4c	0.09340	0.25000	0.41899	1	4c	0.08410	0.25000	0.44136	1
O	4c	0.09761	0.25000	0.74805	1	4c	0.13876	0.25000	0.76311	1
O	4c	0.44605	0.25000	0.21284	1	4c	0.47816	0.25000	0.18800	1
O	8d	0.16522	0.04526	0.28581	1	8d	0.16884	0.05095	0.26912	1

Table S3. Structural parameters obtained from Rietveld refinement of the XRD pattern of R-LFP. **Phase $LiFePO_4$:** Space group: *Pnma*, a=10.325672 Å, b=6.006433 Å, c=4.693817 Å, α=β=γ=90°.

Atoms	Site	Wyckoff positions			Occupancy
Li	4a	0	0	0	0.98002
Fe	4a	0	0	0	0.01998
Fe	4c	0.28198	0.25000	0.97324	0.98002
Li	4c	0.28198	0.25000	0.97324	0.01998
P	4c	0.09596	0.25000	0.41435	1
O	4c	0.09430	0.25000	0.73796	1
O	4c	0.45546	0.25000	0.20517	1
O	8d	0.16418	0.04626	0.28415	1

Table S4. The results of calculating average Li^+ diffusion coefficients based electrochemical impedance spectroscopy (EIS) for S-LFP and R-LFP.

	S-LFP	R-LFP
Equation	y=a+bx	
Intercept (a)	41.62277 ± 0.90638	15.25739 ± 0.65512
Slope (b)	125.27699 ± 3.05971	115.58692 ± 2.21153
R-square	0.99702	0.99817
D_{Li} ($cm^2 \cdot s^{-1}$)	3.40291×10^{-15}	3.99739×10^{-15}

Table S5. The cost and profit of recycling 1.0 kg spent $LiFePO_4$ batteries.[1-3]

	Chemical	Price	Dosage	Total
Consumption	S-LFP	1.38 $/kg	1.0 kg	1.38 $
	H_2O_2	0.12 $/L	4 L	0.48 $
	CA	0.66 $/kg	0.666 kg	0.439 $
	LiOH	68.86 $/kg	0.0079 kg	0.544 $
	Electricity	0.11 $/kw·$h^{-1}$	0.87 kw·h^{-1}	0.096 $
Total	2.939 $			
	Chemical	Price	Dosage	Total
Product	R-LFP	12.05 $/kg	0.269 kg	3.241 $
Total	3.241 $			
Profit	0.302 $			

Text S1. Electrochemical impedance spectroscopy (EIS)

The Li^+ diffusion coefficient can be calculated using the diagonal line in the low-frequency region of the EIS test by using the following equation:[4, 5]

$$Z' = K + \sigma\omega^{-1/2} \tag{1}$$

$$D_{Li} = \frac{R^2T^2}{2n^2F^4A^2C^2\sigma^2} \tag{2}$$

Z' and ω appearing in Equation (1) represent the real part of impedance and the angular frequency respectively. σ is the Warburg factor. In Equation (2), D_{Li} denotes lithium-ion diffusion coefficient (cm s^{-1}), R indicates the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), n refers here to the number of charge transfers of $LiFePO_4$ molecule during the lithium intercalation process (1.0), F is the Faraday constant, A refers to the surface area of the electrode pole piece (1.13 cm^2), and C represents the concentration of Li^+ in $LiFePO_4$ (2.28×10^{-2} mol cm^{-3}).

Text S2. Economic analysis

The cost and profit of the recycling process were calculated in detail using 1 kg of used LFP batteries as an example. It is estimated that 269 g of R-LFP active material can be obtained by treating 1 kg of used LFP batteries. The whole recycling process consumes chemicals such as H_2O_2, CA, and LiOH, and recovers LFP as profit. In addition, the cost of electricity is considered. The cost and profit of this strategy are detailed in Table S5.

References

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5. J. Tu, K. Wu, H. Tang, H. Zhou and S. Jiao, *Journal of Materials Chemistry A*, 2017, **5**, 17021−17028.