

Supplemental information

Enabling Sustainable recycling of LiFePO_4 from spent lithium-ion batteries

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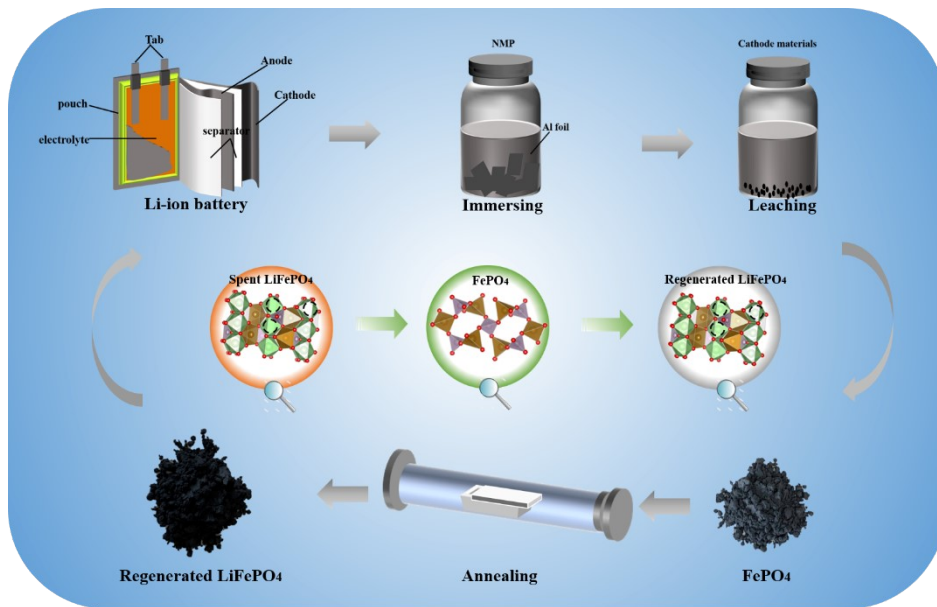


Fig. S1. The presentation of the oxidated leaching for the regeneration LFP cathode material.

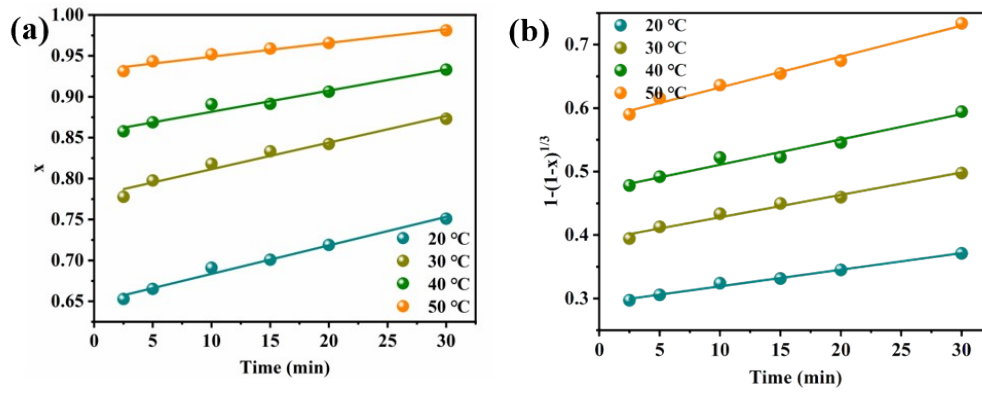


Fig. S2. Kinetics fitting data at different temperatures for (a) external diffusion model, (b) chemical reaction model.

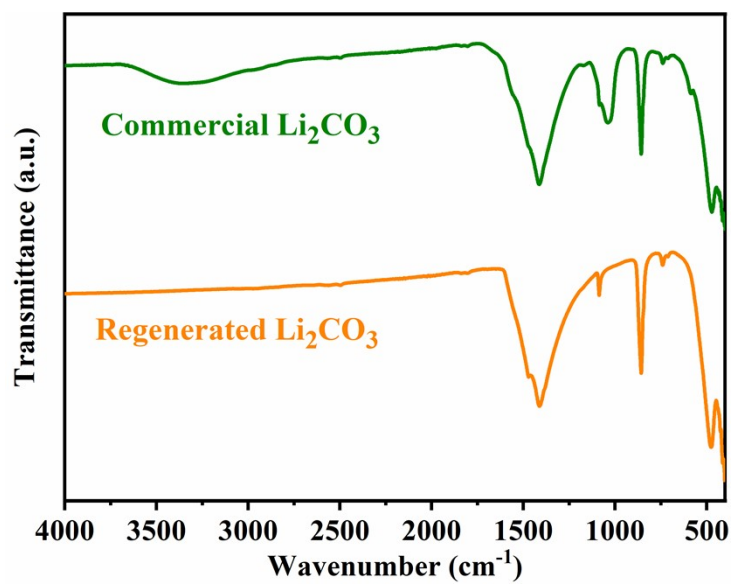


Fig. S3 FT-IR spectra of the samples from the lithium enriched filtrate and that of the commercial Li₂CO₃.

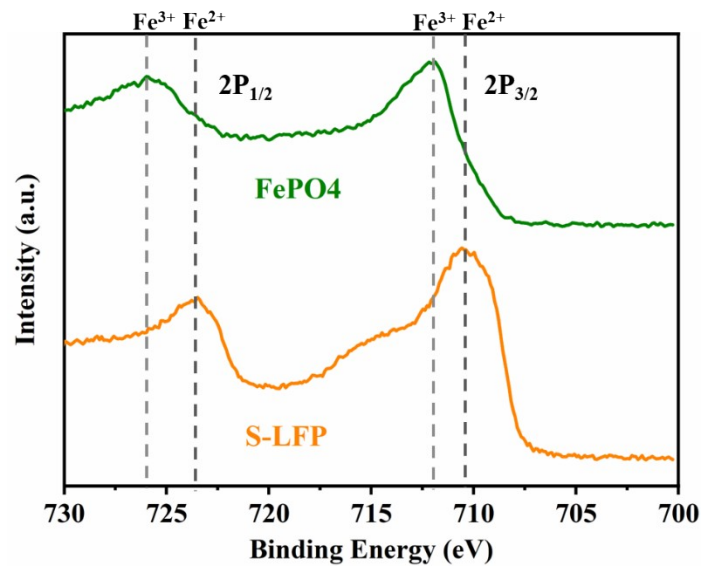


Fig. S4 XPS spectra of Fe 2p for the S-LFP and FePO₄.

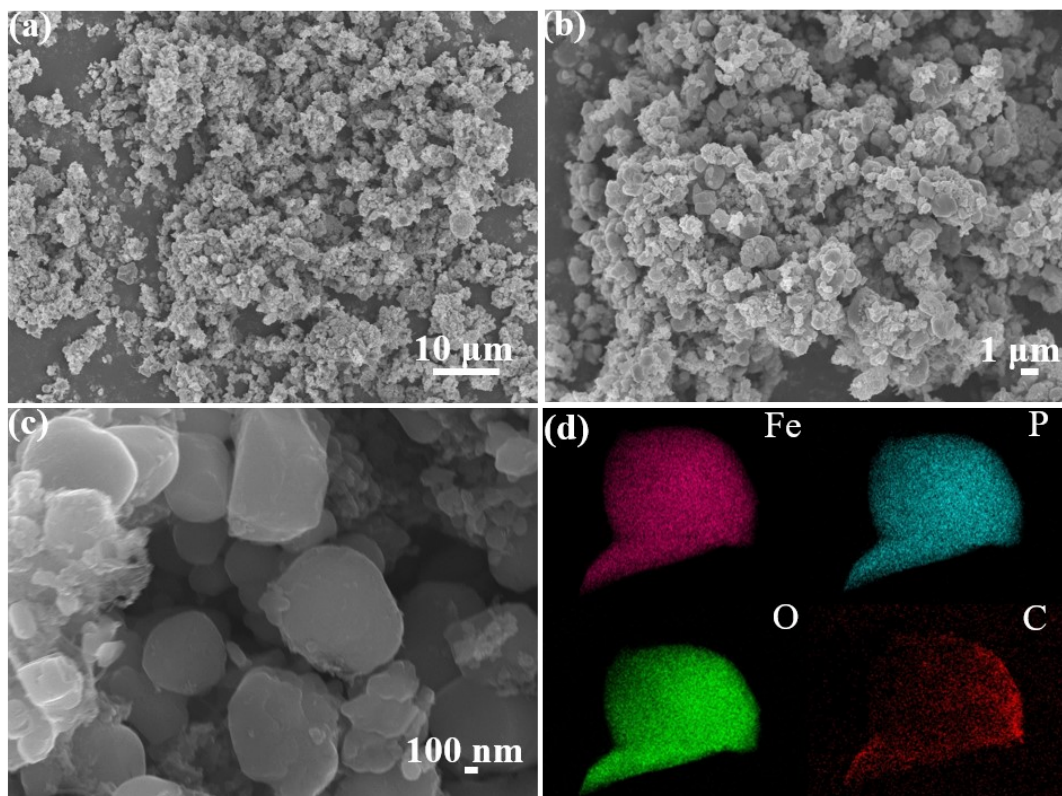


Fig. S5 (a, b, c) SEM images and (d) elemental mapping of the spent LiFePO_4 .

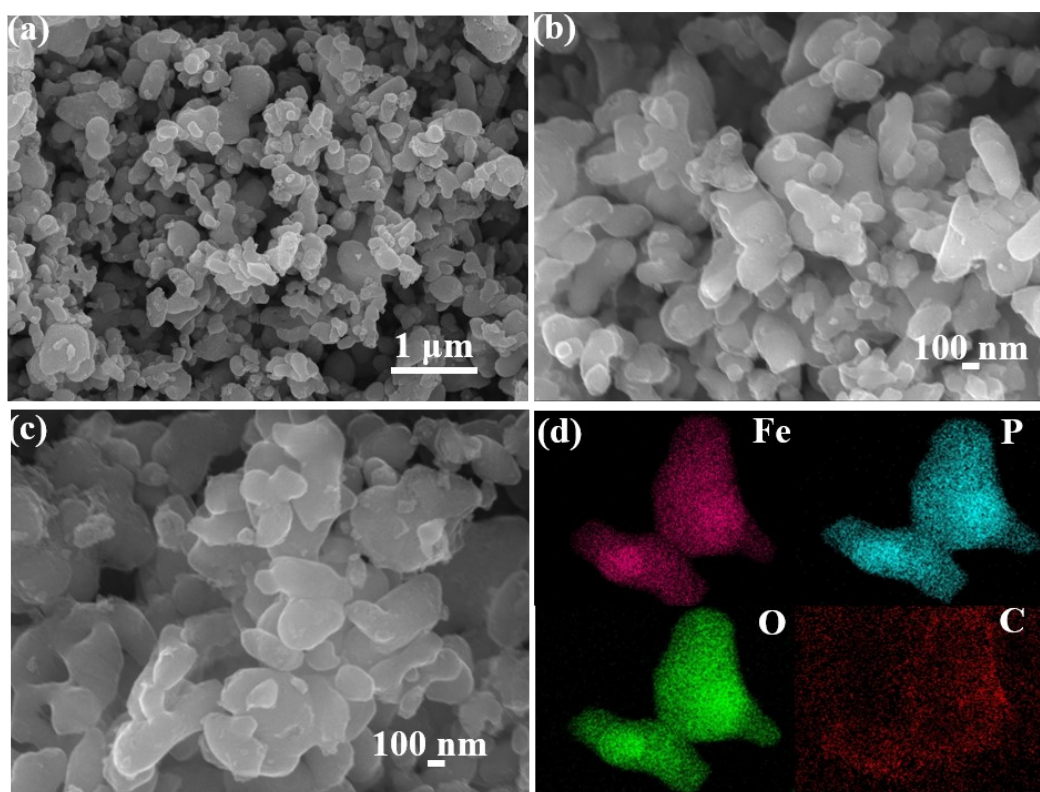


Fig. S6 (a, b, c) SEM images and (d) elemental mapping of FePO₄ by hydrogen peroxide leaching.

Table S1. The main composition of the spent LiFePO_4 cathode materials

Element	Li	Fe	P	Al
Content (wt. %)	3.61	36.34	20.15	0.01

Table S2 Kinetics leaching results at different temperatures and different times

Temperature (°C)	Leaching efficiency (%)						
	Time (min)	2.5	5	10	15	20	30
20		65.2	66.5	69.1	70.0	71.8	75.1
30		77.7	79.7	81.8	83.3	84.2	87.3
40		85.7	86.8	89.0	89.1	90.6	93.3
50		93.1	94.3	95.1	95.8	96.5	98.1

Table S3 Kinetics fitting data of x vs. time at different temperatures

Temperature (°C)	Kinetics fitting data						
	Time (min)	2.5	5	10	15	20	30
20		0.6528	0.6650	0.6911	0.7008	0.7189	0.7510
30		0.7779	0.7975	0.9190	0.8334	0.8421	0.8730
40		0.8577	0.8687	0.8907	0.8913	0.9061	0.9331
50		0.9311	0.9432	0.9518	0.9586	0.965	0.9810

Table S4 Kinetics fitting data of $1-2/3x-(1-x)^{2/3}$ vs. time at different temperatures

Temperature (°C)	Kinetics fitting data						
	Time (min)	2.5	5	10	15	20	30
20		0.0708	0.0743	0.0823	0.0854	0.0916	0.1035
30		0.1146	0.1235	0.1335	0.1416	0.1464	0.1653
40		0.1556	0.1625	0.1776	0.1780	0.1894	0.2132
50		0.2125	0.2234	0.2330	0.2413	0.2504	0.2749

Table S5 Kinetics fitting data of $1-(1-x)^{1/3}$ vs. time at different temperatures

Temperature (°C)	Kinetics fitting data						
	Time (min)	2.5	5	10	15	20	30
20		0.2971	0.3055	0.4340	0.3311	0.3449	0.3709
30		0.3943	0.4128	0.4333	0.4497	0.4595	0.4974
40		0.4779	0.4918	0.5219	0.5227	0.5455	0.5942
50		0.5901	0.6156	0.6360	0.6543	0.6747	0.7334

Table S6 Results of average Li⁺ diffusion coefficient for R-LFP and S-LFP calculated by electrochemical impedance spectroscopy (EIS).

	R-LFP	S-LFP
Equation	Y=a+bx	
Intercept (a)	18.89367 ± 3.484	81.07694 ± 12.63
Slope (b)	31.3281 ± 0.5568	78.76399 ± 2.019
R-square	0.99811	0.99607
D _{Li}	4.66062 × 10 ⁻¹⁵	7.40184 × 10 ⁻¹⁶

Principles and model of leaching kinetics

In the light of the conventional hydrometallurgy process, the classical shrinking core model is generally employed to depict the leaching reaction when the solid granule reacts with the leaching agent, afterwards, the unreacted nucleus will gradually shrink and disappear during the dissolving procedure. The leaching reaction includes the following steps:

- (1) The leaching agent firstly diffuses to the surface of the solid granule in the bulk solutions, referred to as external diffusion.
- (2) The leaching agent then diffuses to the solid-liquid interface of the solid granule through the fluid film, referred to as internal diffusion.
- (3) Finally, the leaching agent reacts with the solid granule, referred to as chemical reaction.

Consequently, the leaching agent diffused into the liquid phase in reverse order.

The reaction rate-controlling steps including external diffusion, internal diffusion and chemical reaction during leaching are shown in the following Eqns.

$$x=k_1t \quad (1)$$

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

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

Where x is the leaching efficiency of lithium, k_1 , k_2 , k_3 is the reaction rate constants, and t is the retention time (min).

Ultimately, the Arrhenius equation (Eq. (4)) was employed to determine the apparent activation energy (E_a) for rate-controlling model¹:

$$k=Ae^{-E_a/RT} \text{ or } \ln k=\ln A-E_a/RT \quad (4)$$

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).

Electrochemical impedance spectroscopy (EIS)

The oblique line in the low frequency region is equivalent to the lithium-ion diffusion rate on behalf of the Warburg impedance, which can be calculated according to the following formula:

$$Z' = K + \sigma \omega^{-1/2} \quad (5)$$

$$D_{Li} = 1/2(RT/n^2F^2AC\sigma)^2 \quad (6)$$

Where Z' is the real part of impedance, ω is the angular frequency, σ is the Warburg factor based on the linearly fitting slope between Z' and $\omega^{-1/2}$ in the low frequency region. In Eqn. (5), D_{Li} is the lithium-ion diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (298 K), n is the quantity of charge transfer per mol in the reaction, F is Faraday constant (96485 C mol^{-1}), A is the electrode surface area (1.54 cm^2), C is the concentration of lithium ion in LFP ($2.28 \times 10^{-2} \text{ mol cm}^{-3}$, estimated by the number of lithium ion in a unit cell).

Economic analysis

Table S7 The materials and energy consumption to dispose of 1 kg spent LiFePO₄ batteries^{2,3}

	Items	Price	Dosage	Total
Leaching	H ₂ O ₂	\$/L	L	\$
		0.162	4.1	0.66
Leaching	Energy cost	\$/kW h	kW h	\$
		0.07	0.38	0.026
Regeneration	LiOH	\$/kg	g	\$
		14.01	4	0.056
Regeneration	Energy cost	\$/kW h	kW h	\$
		0.07	0.49	0.034
Cost				0.776

(1) As listed in Table S7, the cost of reagents for the regeneration process is calculated as follow.

Hydrogen peroxide

$$0.162\$/L \times 4.1 L = 0.66\$$$

Additional LiOH₂

$$14.01\$/kg \times 4 g = 0.056\$$$

(2) The energy consumption for the regeneration process is calculated as follow.

$$0.07\$/kW h \times 0.38 kW h = 0.026\$$$

$$0.07\$/kW h \times 0.49 kW h = 0.034\$$$

Calculation of benefits and profits: Approximate 1.0 kg spent LiFePO_4 batteries is taken as sample, economic assessment in laboratory-scale for spent LIBs recycling is performed based on proposed process. The benefits for the whole process can be obtained from the regeneration of 269g LiFePO_4 , the ultimate profits are calculated as follows.

$$\text{Profits: } 269\text{g} \times 7.7\$/\text{kg} - 1\$ - 0.66\$ - 0.056\$ - 0.026\$ - 0.034\$ = 0.295\$$$

Table S8 The comparison of different recycling processes from spent LiFePO_4 cathode materials.

Recycling Process	Experimental Conditions	Waste Production	Significance	Ref.
Repair with solid phase annealing	Annealing: 600-800°C for 1 h according to the absence of lithium, NaOH solution	Aluminum-containing alkaline waste liquid	Environmentally friendly recycling process, satisfactory electrochemical performance	4
Healing with relithiation and short annealing	Relithiation: 80 °C for 5 h Annealing: 600 °C for 2 h	Salt-containing wastewater	Safe and low-cost regenerative process, excellent electrochemical performance	5
Acid leaching and hydrothermal synthesis	Leaching: 70 °C for 2 h Hydrothermal synthesis: 200 °C for 6 h Calcination: 200 °C for 6 h	Salt-containing wastewater Graphite residue	Short and efficient recycling approach good electrochemical performance	2
Organic acid leaching	Leaching: 60 °C for 0.5 h Li_2CO_3 recovery: concentration by evaporation	Sodium acetate solution Ferric hydroxide precipitation	Selective leaching with a high recovery rate	6
Redox targeting-based process	Electrolysis: react in the $[\text{Fe}(\text{CN})_6]^{3-}$ electrolyte LiOH recovery: concentration by evaporation	$[\text{Fe}(\text{CN})_6]^{3-}$ toxic wastewater	No corrosive chemicals and minimal chemical consumption	7
Oxidation leaching	1.4 times amount of theoretical $(\text{NH}_4)_2\text{S}_2\text{O}_8$ Li_2CO_3 recovery: adding NaCO_3	$(\text{NH}_4)_2\text{SO}_4$ solution	One-step oxidation leaching with separating three materials	3
Oxidation leaching	H_2O_2 dosage of Vol. %15 Li_2CO_3 recovery: inletting CO_2 gas	/	Green and efficient process, excellent electrochemical performance	This work

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