

Supporting information

Start from the source: Direct treatment of degraded LiFePO₄ cathode for efficient recycling of spent lithium-ion batteries

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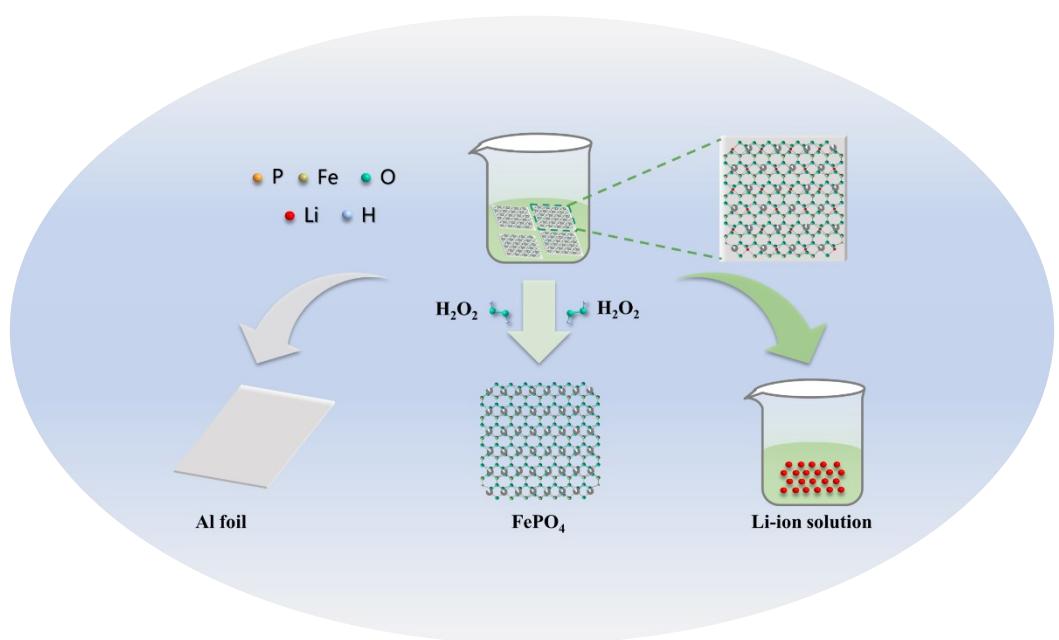


Fig. S1 The schematic diagram of one-step oxidation leaching by hydrogen peroxide.

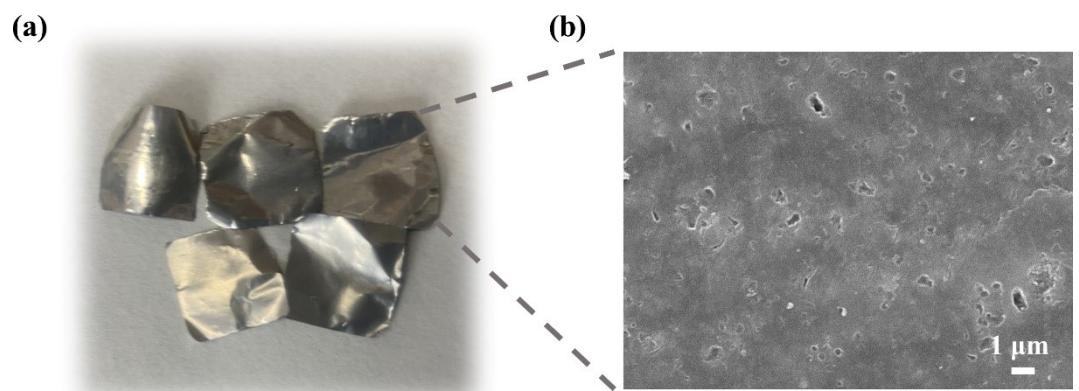


Fig. S2 (a) The picture and (b) SEM image of the stripped aluminum foil.

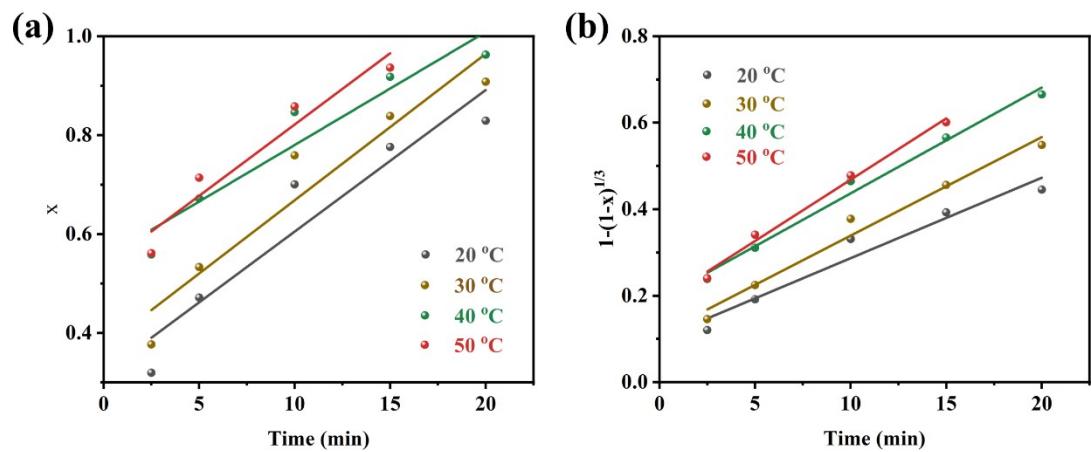


Fig. S3 Kinetics fitting diagram at different temperature for (a) external diffusion model and (b) chemical reaction model.

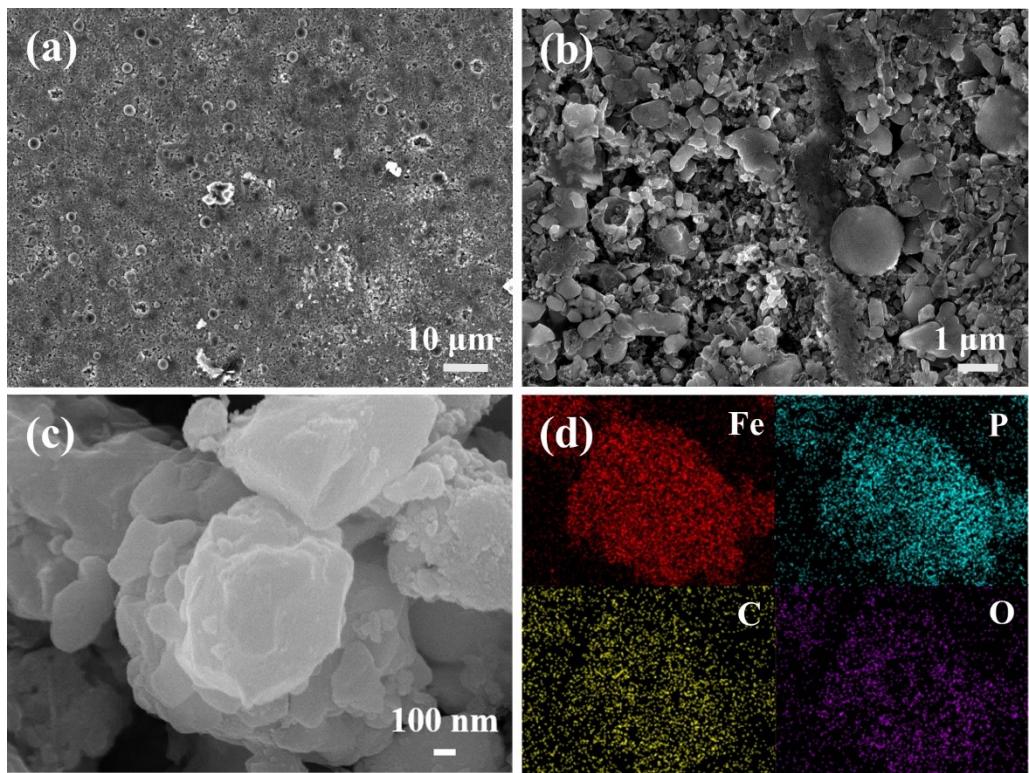


Fig. S4 (a, b, c) SEM images and (d) Elemental mapping of the spent LiFePO₄ cathode sheets.

Table S1 The main elements content of the spent LiFePO₄ cathode sheets.

Element	Li	Fe	Al	P
Content (wt. %)	4.35	42.13	28.56	21.71

Text S1 Principle and calculation formula of leaching kinetics

In the process of leaching by hydrometallurgy, the reaction principle between solid reactants and leaching solution confirms to be typical shrinking core models. According to this theory, the chemical reaction step mainly takes place at the interface of the unreacted nucleus, and the leaching process is gradually from the external solution to the interior of the unreacted particle, while the diffusion process of the leachate is opposite. The leaching steps are as follows:

- (1) The leaching agent diffuses through the solution to the surface of the solid reactant particles, represented as external diffusion step.
- (2) The leaching agent passes through the solid product layer to the surface of the unreacted nucleus, represented as internal diffusion step.
- (3) The leaching agent reacts on the surface of the solid reactant, represented as chemical reaction step.
- (4) The leachate reaches the surface of the solid reactant particles from the reaction interface through the solid product layer.
- (5) The leachate diffuses from the surface of the solid reactant particles back into the solution.

When external diffusion, internal diffusion and chemical reaction are respectively the rate control steps of leaching process, the leaching kinetics equations are shown in equations (1) – (3).

$$x = k_1 t \quad (1)$$

$$1 - 2/3x - (1 - x)^{2/3} = k_2 t \quad (2)$$

$$1 - (1 - x)^{1/3} = k_3 t \quad (3)$$

Where x represents the leaching efficiency of Li (%), k_1 , k_2 , k_3 represent the reaction rate constants in each situation (min^{-1}), t represents the oxidation time (min).

Table S2 The leaching result of Li⁺ at different temperatures and different time.

Temperature(°C) Time (min)	Leaching efficiency (%)					
	2.5	5	10	15	20	30
20	31.9	47.2	70.1	77.6	82.9	84.1
30	37.7	53.3	75.9	83.9	90.8	88.9
40	55.9	67.2	84.7	91.8	96.3	96.8
50	56.1	71.4	85.8	93.7	94.5	94.1

Table S3 The kinetics fitting data of x at different temperatures varies with time.

Kinetics fitting data						
Temperature(°C) Time (min)	2.5	5	10	15	20	30
20	0.3194	0.4715	0.7005	0.7760	0.8291	0.8410
30	0.3768	0.5332	0.7591	0.8388	0.9078	0.8890
40	0.5587	0.6720	0.8465	0.9180	0.9625	0.9680
50	0.5613	0.7138	0.8580	0.9365	0.9453	0.9410

Table S4 The kinetics fitting data of $1-2/3x - (1-x)^{2/3}$ at different temperatures varies with time.

Kinetics fitting data						
Temperature(°C) Time (min)	2.5	5	10	15	20	30
20	0.0133	0.0320	0.0854	0.1138	0.1393	0.1458
30	0.0192	0.0428	0.1068	0.1446	0.1907	0.1764
40	0.0479	0.0764	0.1450	0.1993	0.2563	0.2539
50	0.0484	0.0898	0.1558	0.2165	0.2257	0.2211

Table S5 The kinetics fitting data of $1 - (1-x)^{1/3}$ at different temperatures varies with time.

Kinetics fitting data						
Temperature(°C) Time (min)	2.5	5	10	15	20	30
20	0.1204	0.1915	0.3309	0.3927	0.4451	0.4582
30	0.1458	0.2243	0.3778	0.4558	0.5482	0.5194
40	0.2387	0.3104	0.4646	0.5656	0.6653	0.6825
50	0.2402	0.3410	0.4783	0.6010	0.6204	0.6107

Table S6 The fitting data of different kinetic models at different leaching temperatures.

Kinetic models	20 °C		30 °C		40 °C		50 °C	
	Slope	R ²						
External diffusion	0.02863	0.89900	0.02962	0.91392	0.02286	0.91748	0.02885	0.93373
Internal diffusion	0.00737	0.97709	0.00985	0.99224	0.01198	0.99826	0.01332	0.99692
Chemical reaction	0.01860	0.95161	0.02278	0.97830	0.02447	0.98948	0.02833	0.99156

Text S2 Electrochemical impedance spectroscopy (EIS)

The semi-circle part and the straight part of the Nyquist plot represent the high frequency region and the low frequency region, respectively. The low frequency region line is equivalent to the lithium-ion diffusion impedance, and the lithium-ion diffusion coefficient can be obtained by slope calculation. Equations are as follows:

$$Z' = K + \sigma\omega^{-1/2} \quad (4)$$

$$D_{Li} = \frac{R^2 T^2}{2n^2 F^4 A^2 C^2 \sigma^2} \quad (5)$$

In Equation (4), Z' represents the real part of impedance, σ represents the Warburg coefficient, ω is the angular frequency. In Equation (5), D_{Li} represents the lithium-ion diffusion coefficients (cm s^{-1}), R represents gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T represents the absolute temperature (K), n represents the electron transfer number of LiFePO_4 molecules during lithium intercalation (1.0), F represents Faraday constant (96485 C mol^{-1}), A represents the surface area of the electrode (1.54 cm^2), C represents the concentration of Li^+ in LFP ($2.28 \times 10^{-2} \text{ mol cm}^{-3}$), σ represents the slope of $Z' \sim \omega^{-1/2}$.

Table S7 The data from calculating lithium-ion diffusion coefficients based the lines of $Z' \sim \omega^{-1/2}$ for R-LFP and S-LFP

	R-LFP	S-LFP
Slope	31.2203 ± 0.3922	126.3310 ± 0.9648
Intercept	145.7437 ± 0.4241	332.2629 ± 1.0431
R^2	0.9987	0.9995
$D_{Li} (\text{cm}^2 \text{ s}^{-1})$	2.9471×10^{-14}	1.7999×10^{-15}

Text S3 Economic analysis

Based on 1.0 kg spent LiFePO₄ batteries, the total investment and profits in the recycling process were calculated in detail. It is estimated that 358 g cathode sheets could be obtained from the treatment of 1.0 kg spent LiFePO₄ batteries, including 40.57 g aluminum foil. According to the button cells which are composed of R-LFP powder, super P and polyvinylidene fluoride (PVDF) binder in a ratio of 8:1:1 mixed with appropriate N-methyl pyrrolidone (NMP) as solvent, 285.69 g R-LFP could be gained in the end.

Chemicals such as H₂O₂ (20% vol), LiOH and Na₂CO₃ were consumed in the whole recycling process, and R-LFP, Li₂CO₃ and aluminum foil were recycled and considered as profits. In addition, the costs of electricity and wastewater treatment are also taken into account in the economic analysis. The cost and profit of this recycling strategy are detailed in Table S8.

Table S8 The cost and profit of recycling 1.0 kg spent LiFePO₄ batteries.

	Chemical	Price	Dosage	Total
Consumption	S-LFP	1 \$/kg	1.0 kg	1.0 \$
	H ₂ O ₂ (20% vol)	0.14 \$/L	19 L	2.66 \$
	LiOH	14.42 \$/kg	0.076 kg	1.096 \$
	Na ₂ CO ₃	0.225 \$/kg	0.092 kg	0.021 \$
	Electricity	0.08 \$/kw·h ⁻¹	2.2 kw·h ⁻¹	0.176 \$
	Wastewater	0.10 \$/m ³	19 L	1.9 \$
Total			6.853 \$	
	Chemical	Price	Dosage	Total
Product	R-LFP	23.29 \$/kg	0.286 kg	6.661 \$
	Li ₂ CO ₃	24.94 \$/kg	0.064 kg	1.596 \$
	Aluminum foil	3.71 \$/kg	0.041 kg	0.152 \$
Total			8.409 \$	
Profit			1.556 \$	

References

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