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Supporting information

Regeneration of $LiFePO_4$ from spent lithium-ion battery by a facile process featuring acid leaching and hydrothermal synthesis

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The XRD pattern and composition of the spent LiFePO4 cathode material

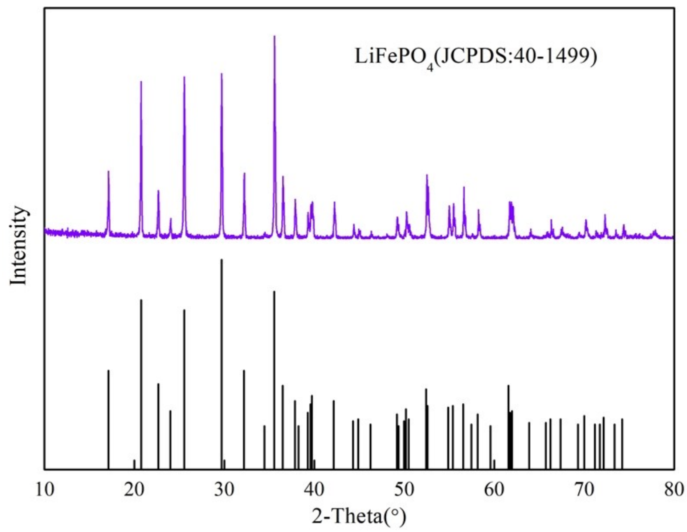

Fig. S1 The XRD pattern of the spent $LiFePO_4$ cathode material

Table S1 The main composition of the spent $LiFePO_4$ cathode material

Content	Li	Fe	P	Al
Composition (wt.%)	3.6	30.5	17.3	0.01

Reaction happens in solution

Table S2 Reaction happens in Li-P-Fe-H_2O system[1, 2]

No.	Reactions
Eq.S1	$Li_3PO_4+2H^+=LiH_2PO_4+2Li^+$
Eq.S2	$Li_3PO_4+2H^+=H_2PO_4^-+3Li^+$
Eq.S3	$Li_3PO_4+4H^++2e=LiH_2PO_3+H_2O+2Li^+$
Eq.S4	$Li_3PO_4+3H^+=H_3PO_4+3Li^+$
Eq.S5	$LiH_2PO_4+2H^++2e=LiH_2PO_3+H_2O$
Eq.S6	$LiOH+H^+=Li^++H_2O$
Eq.S7	$Fe^{3+}+e=Fe^{2+}$
Eq.S8	$FePO_4+2H^+=Fe^{3+}+H_2PO_4^-$
Eq.S9	$FePO_4+3H^+=Fe^{3+}+H_3PO_4+2H_2O$
Eq.S10	$FePO_4+2H^++e=Fe^{2+}+H_2PO_4^-$
Eq.S11	$FePO_4+3H^++e=Fe^{2+}+H_3PO_4$
Eq.S12	$Fe(OH)_3+2H^++HPO_4^{2-}=FePO_4+3H_2O$
Eq.S13	$Fe(OH)_3+H^++e=Fe(OH)_2+H_2O$
Eq.S14	$Fe(OH)_3+3H^+=Fe^{3+}+3H_2O$
Eq.S15	$Fe(OH)_2+2H^+=Fe^{2+}+2H_2O$
Eq.S16	$2H^++2e=H_2$
Eq.S17	$O_2+4e+4H^+=2H_2O$

Shrinking core model

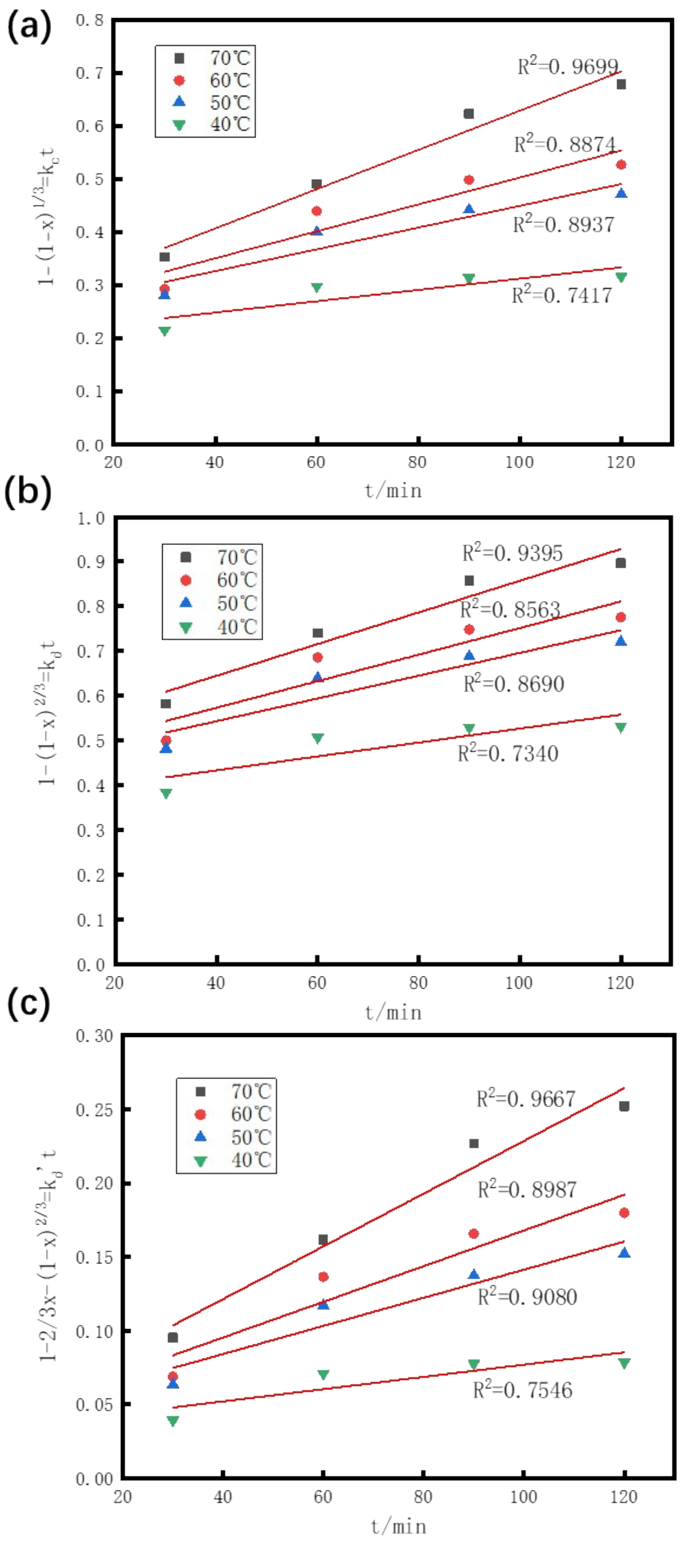

Fig. S2 Fitting curves of different kinetic equations with shrinking core model

In the study of liquid-solid reaction kinetics, the most widely used is the shrinking core model. The reaction consists of five steps: 1) The acid diffuses to the surface of the solid particles; 2) The acid diffuses inside the product layer; 3) The acid reacts with the reaction nucleus at the reaction interface; 4) The product diffuses inside the product layer; 5) Product Diffusion from the product layer to the outside. Among them, the first and fifth steps are the external diffusion control step, the second and fourth steps are the internal diffusion control step, and the third step is the chemical reaction control step. The reaction kinetics equation of the chemical reaction control model is shown in Eq. S18. The diffusion control model is divided into external diffusion control model and internal diffusion control model, the reaction kinetic equations are as shown in Eq. S19 and Eq.S20, respectively.[3, 4]

$$1-(1-x)^{\frac{1}{3}}=k_c t \tag{Eq.S18}$$

$$1-(1-x)^{\frac{2}{3}}=k_d t \tag{Eq.S19}$$

$$1-\frac{2}{3}x-(1-x)^{\frac{2}{3}}=k_d' t \tag{Eq.S20}$$

Where x is the metal leaching rate at the corresponding time t (min); k_c is the chemical reaction rate constant; k_d and $k_{d'}$ are the external diffusion reaction rate constant and internal diffusion reaction rate constant, respectively. Taking Li^+ as an example, the leaching efficiency is fitted according to the above equation, and the result is shown in Fig.S2. It can be seen from Fig.S2 that for the reaction kinetic equations (Eq.S18-S20), the fitting degree R^2 varies from 0.7 to 0.97, and the average fitting degree is not high, which may be due to leaching process is accompanied by other redox reactions.[3, 4]

The peak dates of Fe2p and C1s

Table S3 the peak datas of Fe2p [5-8]

Name	Peak BE	Height CPS	Height ratio	Area CPS.eV	Area ratio	FWHM fit param(ev)	L/G Mix(%) product	Tail max(%)	Tail height(%)	Tail exponent (%)	Valence	Ratio
Fe2p3 Scan A	708.46	1422.30	0.27	2582.30	0.32	1.74	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	7.24
Fe2p3 Scan B	709.10	5031.96	0.94	7149.86	0.89	1.36	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	20.14
Fe2p3 Scan C	710.24	5345.15	1.00	8016.81	1.00	1.44	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	22.62
Fe2p3 Scan D	711.30	2847.93	0.53	4496.22	0.56	1.52	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	12.67
Fe2p3 Scan E	715.81	1397.91	0.26	2317.32	0.29	1.59	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	6.56
Fe2p3 Scan F	711.15	784.01	0.15	1237.77	0.15	1.52	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+3	3.39
Fe2p3 Scan G	712.13	1814.89	0.34	2435.50	0.30	1.29	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	6.79
Fe2p3 Scan H	713	1240.14	0.23	1664.21	0.21	1.29	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+3	4.75
Fe2p3 Scan I	714.82	908.98	0.17	1219.81	0.15	1.29	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+3	3.39

Fe2p3 Scan I	713.91	1789.69	0.33	3531.87	0.44	1.89	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+2	9.95
Fe2p3 Scan I	717.28	507.97	0.1	882.16	0.11	1.67	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed	+3	2.49

Table S4 the peak datas of C1s [6-8]

Name	**Peak BE**	**Height CPS**	**Height ratio**	**Area CPS.eV**	**Area ratio**	**FWHM fit param(ev)**	**L/G Mix(%) product**	**Tail max(%)**	**Tail height(%)**	**Tail exponent (%)**
C1s	284.60 C-C	32066.78	1.00	45406.64	1.00	1.36 0.5 : 3.5	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed
C1s Scan A	285.54 C-O-C	6685.48	0.21	22487.68	0.50	3.23 0.5 : 3.5	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed
C1s Scan B	288.60 O-C=O	1537.45	0.05	3173.90	0.07	1.98 0.5:3.5	30.00 fixed	100.00 fixed	0.00 fixed	0.0000 fixed

Economic analysis

TableS5 The cost to treat 1 ton of spent LiFePO4 batteries

	Items	**Price**	**Dosage**	**Total**
Acid leaching		\$/t	t	\$
	H_2SO_4	76.1265	1.57	119.519
		\$/kW·h	kW·h	\$
	Energy cost	0.07	380	26.6
Hydrothermal reaction		\$/t	t	\$
	LiOH	6743.792	0.120	809.255
	$FeSO_4$	4435.753	0.024	106.458
	Glucose	520.054	0.030	15.602
		\$/kW·h	kW·h	\$
	Energy cost	0.07	490	34.3
Cost				1111.733

Calculation of costs:

(a) The cost of raw materials. The cost of spent $LiFePO_4$ battery is calculated at \$306.536 /ton.

(b) The cost of reagents. According to the price and dosage of the reagents listed in Table S5, the cost of reagents for the recovery process is calculated as follow.

1- acid leaching:

$76.1265/t * 1.57 t = $119.519

2-hydrothermal reaction:

$6743.792 /t * 0.12 t + $4435.753 /t * 0.024 t + $520.054 /t * 0.03 t = $931.315

(c) The cost of energy. According to Table S5, the cost of energy for the recovery process is calculated as follow.

1- acid leaching:

$0.07 /kW·h * 380 kW·h = $26.6

2-hydrothermal reaction:

$0.07 /kW·h * 490 kW·h = $34.3

The cost to treat 1 ton of spent LiFePO4 batteries:

$119.519 + $26.6 + $931.315 + $34.3 = $1111.733

The total costs:

$1111.733+ $306.536 = $1418.269

Calculation of benefits and profits: When recycling of 1 ton of spent $LiFePO_4$ battery, 372.88 kg $LiFePO_4$ can be obtained and1 ton of $LiFePO_4$ is 7283.29$, the benefits and profits are calculated as follows.

Benefits:

7283.29 $/t * 372.88 kg = $2715.793

Profits:

$2715.793 - $1418.269 = $1297.524

Table S6 The comparison of different methods for recycling of spent LFP cathode material

Method	Chemicals consumption	Energy Consumption	Waste production	Product	Ref.
Acid leaching and hydrothermal synthesis	2 M H_2SO_4, glucose, LiOH and $FeSO_4$ according to the absence in leaching solution	✓ Leaching: 70 °C for 2h ✓ Hydrothermal synthesis: 200 °C for 6h ✓ Calcination: 200 °C for 6h	✓ Salt-containing wastewater ✓ Graphite residue	$LiFePO_4$	This work
Sulfuric acid leaching	0.3 M H_2SO_4, H_2O_2 (H_2O_2/Li molar ratio 2.07), NaOH and Na_3PO_4 (The amount is not mentioned)	✓ Leaching: 60 °C for 2h ✓ $FePO_4$ preparation: 600 °C for 4h ✓ Li_3PO_4 preparation: concentration by evaporation	✓ CO_2: C remove from leaching residue to purify $FePO_4$ ✓ Sediment: Mixture of $Al(OH)_3$ and $Fe(OH)_3$	$FePO_4$ Li_3PO_4	9
Oxidizing leaching	1.05 times theoretical amount of $Na_2S_2O_8$	✓ Li_2CO_3 preparation: concentration by evaporation	✓ Na_2SO_4 solution ✓ Aluminum slag	$FePO_4$ Li_2CO_3	2
Organic acid leaching	0.8 mol·L^{-1} CH_3COOH, 6 vol% H_2O_2, NaOH and saturation Na_2CO_3 solution	✓ Leaching: 60 °C for 0.5 h ✓ Li_2CO_3 preparation: concentration by evaporation	✓ CH_3COONa solution ✓ $Fe(OH)_3$ precipitation	$FePO_4$ Li_2CO_3	10
Molten salt Method	0.5 M H_3PO_4	✓ Molten salt reaction: 750 °C under an Ar atmosphere	✓ CO_2 emission in Molten salt reaction ✓ Na_3PO_4 solution	Fe/Fe_3O_4 powder Li_3PO_4	11
Repair by solid-state annealing	Li_2CO_3 according to the absence of lithium of spent cathode material, NaOH solution	✓ 600~800 °C for 1 h	✓ Aluminum-containing alkaline waste liquid	$LiFePO_4$	12
Repair by relithiation and short annealing	0.2 M LiOH, 0.08 M citric acid, Li_2CO_3, Dimethyl carbonate (DMC) and N-Methyl-2-pyrrolidone (NMP)	✓ Relithiation: 80 °C for 5 h ✓ Annealing: 600 °C for 2 h	✓ Salt-containing wastewater	$LiFePO_4$	13

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