Supporting Information

Direct regeneration of spent $LiFePO_4$ cathode materials assisted with a bifunctional organic lithium salt

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Text S1 Experimental

Materials

The relevant reagents employed in this process were analytic grade, including Lithium citrate($Li_3C_6H_5O_7 \cdot 4H_2O$), ethylene glycol($C_2H_6O_2$), dimethyl carbonate (DMC), N-methyl-pyrrolidone (NMP), etc. The above chemicals were sourced from Aladdin Chem. Co., Ltd and used without further purification. Spent $LiFePO_4$ pouch batteries were supplied by Zhuzhou Smelter Group Co., LTD.

Degraded $LiFePO_4$ cathode materials harvesting

The cells were first discharged in the saturated NaCl solution for 24 h and then disassemble and sort manually to get the battery shell, spent LFP anode sheets, spent LFP cathode sheets, separator and so on. The cathode sheets were washed with DMC and dried. After drying, these sheets were immersed in an appropriate amount of deionized water for 30 minutes to ensure complete detachment of the active substance from the collector. The resultant spent LFP (S-LFP) powders were separated, dried for regeneration. The main pretreatment process was shown in Figure S1.

$LiFePO_4$ regeneration

The regeneration of S-LFP was carried out by the method of hydrothermal relithiation. For the hydrothermal relithiation treatment, 0.004 mol of lithium citrate was dissolved in 40 ml of ethylene glycol within a 100 mL reactor to prepare the lithium citrate solution. The above 0.5g of S-LFP was then added for a hydrothermal reaction. In order to explore the optimal regeneration parameters, the effects of different reaction temperatures (100-180 °C) and reaction times (1-12 h) on the physical structure and electrochemical performances of regenerated LFP cathode materials were investigated. Following the reaction, the regenerated LFP (R-LFP) were repeatedly washed with deionized water and dried.

Materials characterization

The element contents of spent and regenerated samples was evaluated by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima-3000DV, USA). The crystal structures of various powders throughout the regeneration process were determined by X-ray powder diffraction (XRD, Ultima IV, Japan) employing Cu Kα radiation. The identification of chemical groups or bonds present in cathode powders was accomplished via Fourier transform infrared spectroscopy (FTIR, VERTEX 70, Germany) and Raman spectroscopy(Raman, Alpha300R, Germany). Surface compositional studies of related materials were undertaken using X-ray photoelectron spectroscopy (XPS, Thermo Scientific

Nexsa, England). The surface morphologies of degraded, regenerated LFP were observed by scanning electron microscope (SEM, ZEISS Sigma 300, Germany). The microstructure, lattice fringe of the powders were examined by high-resolution transmission electron microscopy with energy dispersive spectroscopy (HRTEM-EDS, FEI TitanG260-300, USA).

Electrochemical characterization

The regenerated lithium iron phosphate cathode powder was mixed with Super P and polyvinylidene fluoride(PVDF) in NMP according to the mass ratio of 8:1:1 to obtain a uniform slurry. The resulted slurry is coated on the aluminum foil, followed by vacuum drying at 120 °C for 6 h. The dried electrode sheet is cut into a cathode electrode sheet with a diameter of 14 mm, thereafter assembling button batteries within an argon-filled glove box. The $LiFePO_4$ electrode sheet was used as the cathode electrode, while the anode electrode was lithium metal. The electrolyte comprised 1 mol L^{-1} lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture of ethyl carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) in equal volume proportions. Galvanostatic charge-discharge was carried out in the potential range of 2.5–4.1 V with the assembled cells. The cells were cycled with activation for 3 cycles at 0.1 C followed by extended cycling at higher rates. Electrochemical evaluations, including cyclic voltammetry (CV) were conducted on both R-LFP and S-LFP utilizing an electrochemical workstation (DH 7000, Donghua Testing Technology Co., Ltd).

Text S2 Calculation of Gibbs Free Energy

$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4 \quad E(FePO_4/LiFePO_4) = 0.24\ V \qquad \text{(Equation S1)}$$

$$C_6H_5O_7^{3-} - 2e^- \rightarrow C_5H_4O_5^{2-} + CO_2 + H^+ \quad E(C_5H_4O_5^{2-}/C_6H_5O_7^{3-}) = -0.43\ V \qquad \text{(Equation S2)}$$

$$2FePO_4 + 2Li^+ + C_6H_5O_7^{3-} \rightarrow 2LiFePO_4 + C_5H_4O_5^{2-} + CO_2 + H^+ \qquad \text{(Equation S3)}$$

$E(C_5H_4O_5^{2-}/C_6H_5O_7^{3-}) = -0.43\ V$ (versus SHE) was calculated based on the Nernst equation, where E^{θ} is obtained from literature (- 0.18 V)[1], n is the number of moles of electrons, R is the gas constant, and T is temperature in Kelvin.

$$E = E^{\theta} - \left(\frac{RT}{ZF}\right) \times ln\left(\frac{C_{red}}{C_{ox}}\right) \qquad \text{(Equation S4)}$$

$$= E^{\theta} - \left(\frac{RT}{ZF}\right) \times ln\left(\frac{C_{(C_6H_5O_7^{3-})}}{C_{(C_5H_4O_5^{2-})} \times P_{CO_2} \times C_{H^+}}\right)$$

where the pH value (8.0) was obtained from pH meter. Besides, only the effect of pH value was considered here. The activities of other species were set as 1.[2] The Gibbs free energy for the complete reaction (Equation 1 in the main text) can be calculated using the following equation:

$$\Delta G = -nFE \qquad \text{(Equation S5)}$$

$$= -nF(E(FePO_4/LiFePO_4) - E(C_5H_4O_5^{2-}/C_6H_5O_7^{3-}))$$

Figure S 1 Main pre-treatment process

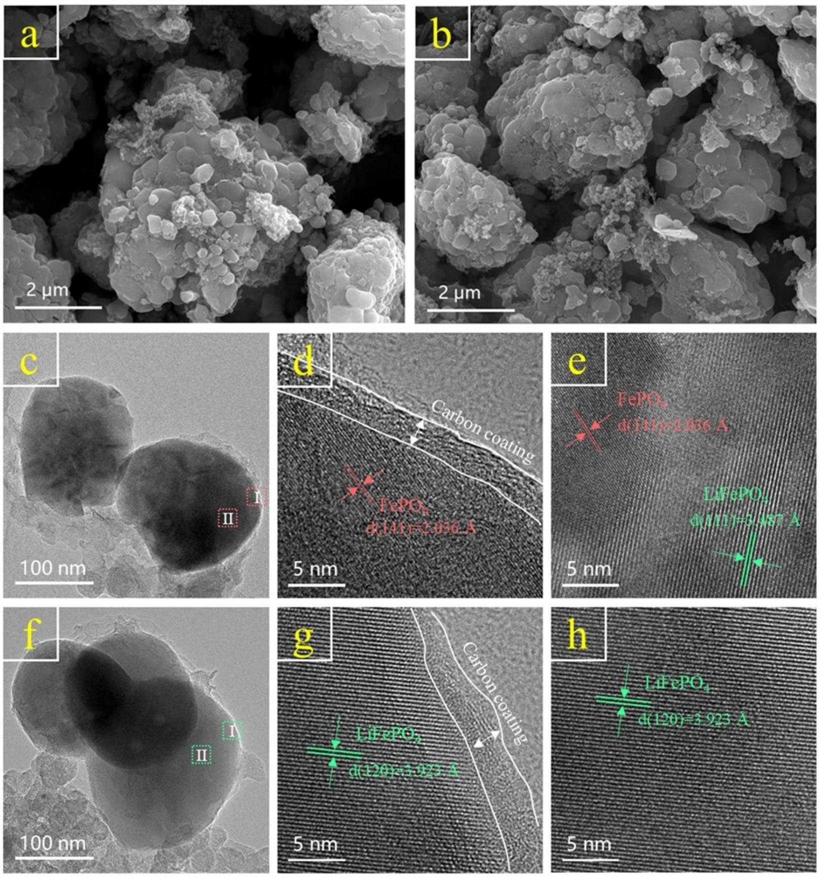

Figure S 2 SEM images of S-LFP (a) and R-LFP (b) materials; TEM images of S LFP (c)–(e) and R-LFP (f)–(h) materials, where (d) and (e) are high resolution images of red rectangle regions I and II in (c), and (g) and (h)

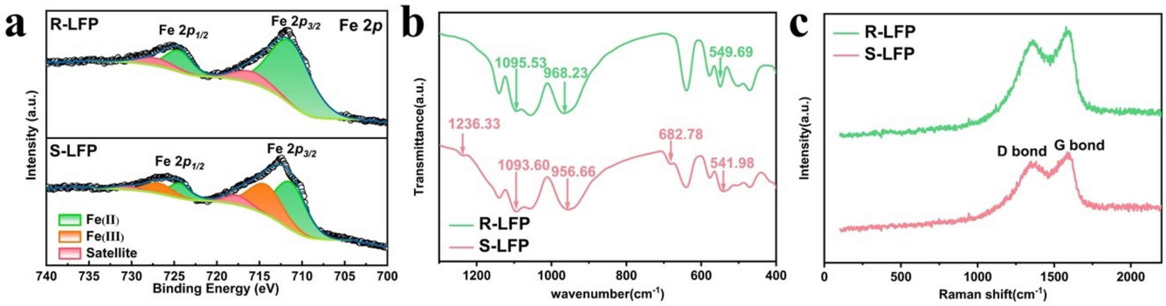

Figure S 3 (a) XPS images of S-LFP and R-LFP; (b) FTIR comparison spectra of S-LFP and R-LFP;(c) Raman spectra of S-LFP and R-LFP

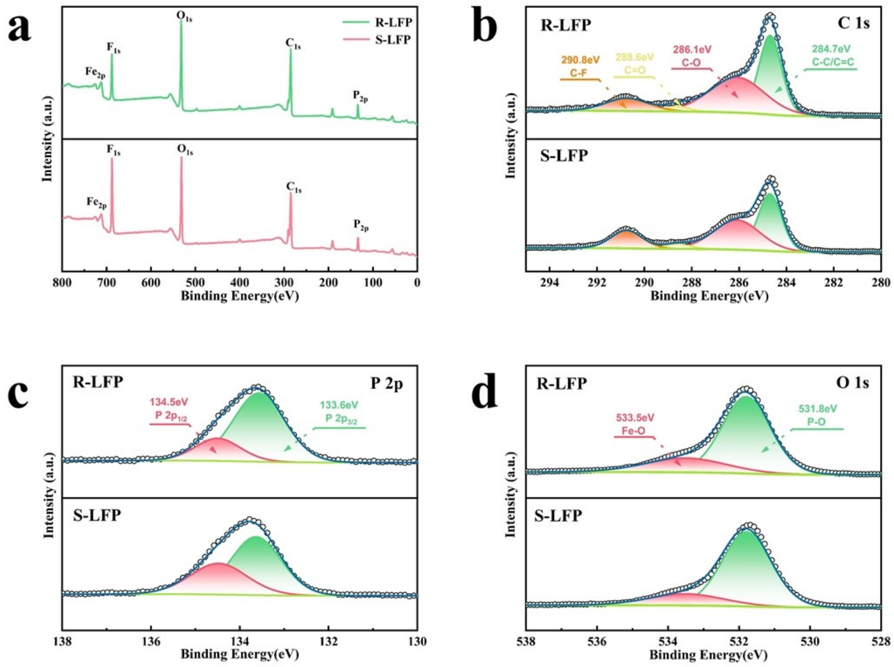

Figure S 4 XPS spectra of S-LFP and R-LFP(a)XPS survey;(b)C 1s;(c) P 2p;(d) O 1s.

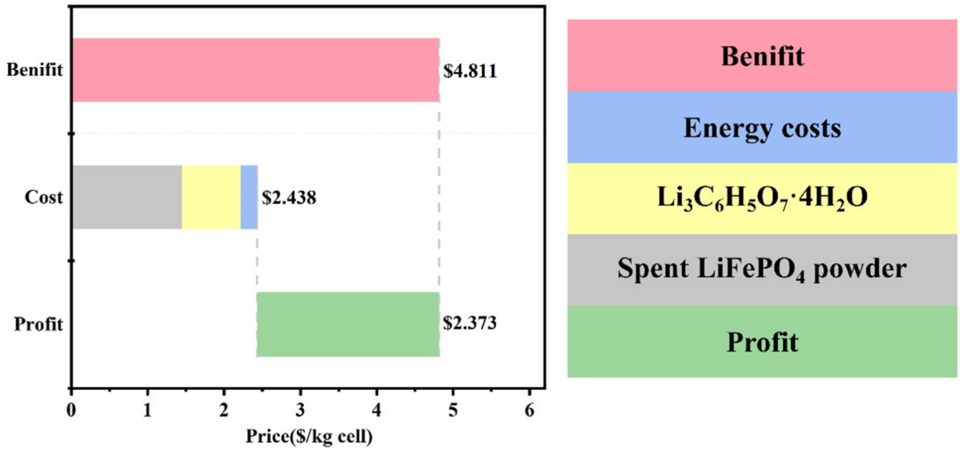

Figure S 5 Cost and profit per kg of spent $LiFePO_4$ cells recycled using the proposed process.

Table S 1 The ICE (Initial Coulombic Efficiency) and the first-cycle charge/discharge specific capacity at 0.1 C rate of S-LFP and regenerated LFP materials at different reaction temperatures.

Materials	S-LFP	100 °C	120 °C	140 °C	160 °C	180 °C
ICE	133.1%	132.6%	123.1%	111.6%	98.7%	99.0%
first-cycle charge specific capacity (mAh g^{-1})	110.1	111.8	122.5	136.7	157.8	156.4
first-cycle discharge specific capacity(mAh g^{-1})	147.2	148.2	150.8	152.5	155.8	154.9

Table S 2 The ICE (Initial Coulombic Efficiency) and the first-cycle charge/discharge specific capacity at 0.1 C rate of S-LFP and regenerated LFP materials at different reaction time.

Materials	S-LFP	1h	3h	5h	7h	12h
ICE	133.1%	122.7%	106.1%	102.7%	98.8%	98.7%
first-cycle charge specific capacity (mAh g^{-1})	110.1	123.1	145.2	151.0	157.9	157.8
first-cycle discharge specific capacity(mAh g^{-1})	147.2	151.1	154.1	155.1	156.0	155.8

Table S 3 Raman data of samples

Samples	I_D	I_G	I_D/I_G
S-LFP	480.18	496.00	0.9681
R-LFP	737.71	745.14	0.9900

Table S 4 Specific cost of our proposed recycling strategy

Items	Price	Dosage	Total	Data Sources
Spent $LiFePO_4$ powder	\$/kg cell	kg cell	\$	wechat
	1.448	1	1.448	
$Li_3C_6H_5O_7 \cdot 4H_2O$	\$/kg	kg	\$	1688
	0.327	2.368	0.774	
Energy costs	\$/kW h	kW h	\$	fgw
	0.108	2	0.216	
Total			2.438	

1\$=7.25￥(Update time: 2024/04/29);
wechat(https://mp.weixin.qq.com/s/0tvUiemXfEOVlJwdLis-cg); 1688(https://www.1688.com/);
fgw(https://fgw.hunan.gov.cn/fgw/xxgk_70899/zcfg/dfxfg/202401/t20240131_32641110.html;)

Calculation of benefits and profits: When recycling of 1kg of spent $LiFePO_4$ battery, 0.8kg $LiFePO_4$ can be obtained and 0.8 kg of $LiFePO_4$ is 4.811\$, the benefits and profits are calculated as follows.

Benefits: 6.014 \$/kg * 0.8 kg = \$4.811

Profits: \$4.811 - \$2.438 = \$2.373

Table S 5 The detail data of XPS

Samples	Elements	Peaks	Area	Percentage(%)	R^2
S-LFP	Fe	Fe^{3+}	28553.81	41.45	0.9948
		Fe^{2+}	40338.33	58.55	
		Sat.	6920.93	-	
	C	C-C/C=C	54068.61	39.45	0.9890
		C-O	55496.88	40.49	
		C=O	4833.82	3.53	
		C-F	22662.20	16.53	
	P	$P_{3/2}$	14373.68	63.15	0.9975
		$P_{1/2}$	8386.36	36.85	
	O	P-O	133859.97	80.82	0.9924
		Fe-O	31767.88	19.18	
R-LFP	Fe	Fe^{2+}	70293.65	100	0.9838
		Sat.	15370.68	-	
	C	C-C/C=C	59119.34	40.86	0.9966
		C-O	63864.63	44.14	
		C=O	3684.83	2.55	
		C-F	18013.77	12.45	
	P	$P_{3/2}$	16569.23	77.54	0.9974
		$P_{1/2}$	4800.69	22.46	
	O	P-O	136612.68	76.42	0.9975
		Fe-O	42151.00	23.58	

Table S 6 The detailed components of a spent LFP battery

Components	Percentage by weight in %
Cathode	30.00
Anode	20.00
Cathode Al foil	10.00
Anode Cu foil	11.00
Separator	5.00
Electrolyte	13.00
Outer shell	10.00
Other components	1.00

Table S 7 The comparison of various direct regeneration strategies for spent LFP cathode materials reported in the literature.

Methods	Reagents	Conditions	Discharge performance	Ref.
Solid state sintering	S-LFP+Li_2CO_3+CNTs+glucose	heated at 350 °C for 2 h, and then heated at 650 °C for 12 h in Ar	155.47 mAh g^{-1} at 0.05 C, remains stable till 800 cycles at 1 C	3
	S-LFP+Li_2CO_3+melamine	heated at 350 °C for 2 h, and then heated at 650 °C for 12 h in Ar	135 mA h g^{-1} at 2C, 99.03% capacity retention after 200 cycles	4
	S-LFP+Li_2CO_3	heated at 700 °C for 8 h in CO_2	131.2 mA h g^{-1} at 1 C, 88.64% capacity retention after 400 cycles	5
Hydrothermal relithiation	S-LFP+LiOH+H_2O_2	hydrothermal at 30 °C for 1 h , then annealing at 700 °C for 10 h	156.6 mA h g^{-1} at 1 C, 84.9% capacity retention after 1000 cycles at 5C	6
	S-LFP+LiOH+L-ascorbic acid+$C_{18}H_{29}SO_3Na$	hydrothermal at 160 °C for 6 h	150.4 mA h g^{-1} at 0.5 C, remains stable till 300 cycles	7
	S-LFP+Li_2SO_4+Na_2SO_3	hydrothermal at 200 °C for 6 h	145.1 mA h g^{-1} at 0.1 C, 99% capacity retention after 100 cycles at 1 C	8
Electrochemical relithiation	Li_2SO_4 as the electrolyte	Three-electrode system	136.5 mAh g^{-1} at 1 C, 95.32 % capacity retention after 300 cycles at 5 C	9
	Li_2SO_4 as the electrolyte	Three-electrode system	135.2 mA h g^{-1} at 1 C, 95.30% capacity retention rate after 500 cycles.	10
	$Li_2C_2O_4$ as lithium source	Functionalized prelithiation separator	146.7 mAh g^{-1} at 1C in the full cell, 90.7 % capacity retention after 292 cycles	11
Our work	S-LFP+$Li_3C_6H_5O_7 \cdot 4H_2O$ + ethylene glycol	hydrothermal at 160 °C for 7 h	142.7 mAh g^{-1} at 1 C, remains stable till 200 cycles	

Reference

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