Electronic Supplementary Information

Facile and efficient recovery of lithium from spent $LiFePO_4$ batteries via air oxidation leaching at room temperature

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Number of pages: 14

Number of figures: 5

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2 Experimental section

2.2 Experimental procedure of selective leaching.

Details for ICP analysis

Table S1 The main operating parameters for ICP-OES analysis

Plasma generation	
Plasma gas	Argon (＞99.99%)

RF/MW power (kW)	1.2
Carrying gas flow (L/min)	1.2
Cool gas flow (L/min)	13
Auxiliary gas flow (L/min)	1.0
Plasma stabilization time (sec)	15
Wavelengths (nm)	Li 670.784, Fe 259.940, P 213.618, Al 308.215, Cu 327.396
Matrix	Li: HNO_3, Fe: HCl, P: H_2O, Al: HCl, Cu: HCl
Concentration of the standard solutions (ppm)	0, 5, 10, 20
Emission registration	
Replicates	2
Replicate read time (sec)	15
Sample uptake parameters	
Sample uptake	Auto
Sample uptake time (sec)	30
Feed pump rate (rpm)	20
Rinse time (sec)	10
Rinse pump rate (rpm)	20
Test pump rate (rpm)	20

Nitric and hydrochloric acid were added to prepare the standard solutions to keep an acidity of 1%. Addition, the acidity of samples was adjusted to the same as the standard solutions by nitric or hydrochloric acid to reduce the matrix effect. In order to avoid possible interference from other elements to the measured elements, the spectral lines of the elements have been filtered. A working curve was determined by 4 different concentrations of the standard solutions and the background equivalent concentration was removed. Then the concentration of different element in the solution was measured.

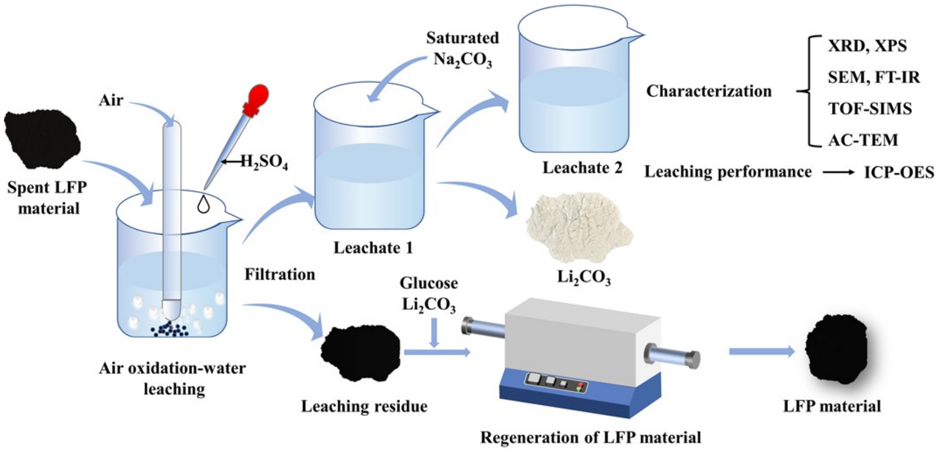

Figure S1. The experimental procedure of the air oxidation-water leaching method

3 Results and discussion

3.1 Thermodynamic analysis

Table S2. $\Delta_f G_T^{\circ}$ (kJ·mol^{-1}) of different species at 25 °C (298.15 K)[12]

Species	$\Delta_f G_T^{\circ}$ (kJ·mol^{-1})	Species	$\Delta_f G_T^{\circ}$ (kJ·mol^{-1})
Li^+	−293.69	PO_4^{3-}	−1018.77
Fe^{2+}	−78.87	Li_3PO_4	−1965.90
Fe^{3+}	−4.61	$FePO_4\cdot 2H_2O$	−1657.45
$Fe(OH)_2$	−492.05	$Fe_3(PO_4)_2\cdot 8H_2O$	−4359.07
$Fe(OH)_3$	−705.58	$LiFePO_4$	−1480.97
H_3PO_4	−1118.92	H_2O	−237.14
$H_2PO_4^-$	−1137.15	Li_2SO_4	-1282.40
HPO_4^{2-}	−1089.13		

Table S3. Equilibrium equations relative to the *E*-pH diagram of Li-Fe-P-H_2O system at 25 °C (298.15 *K*) [12]

No.	Reactions	*E* vs pH equations
1	$2H^+ + 2e = H_2$	$E = -0.0592\ pH$
2	$O_2 + 4e + 4H^+ = 2H_2O$	$E = 1.229 - 0.0592\ pH$
3	$Fe^{3+} + e = Fe^{2+}$	$E = 0.7696 - 0.0592\ lg\ [Fe^{2+}]/[Fe^{3+}]$
4	$FePO_4 \cdot 2H_2O + 3H^+ = Fe^{3+} + H_3PO_4 + 2H_2O$	$pH = -3.482 - 1/3\ lg\ [Fe^{3+}][H_3PO_4]$
5	$FePO_4 \cdot 2H_2O + 3H^+ + e = Fe^{2+} + H_3PO_4 + 2H_2O$	$E = 0.1515 - 0.0592\ lg\ [Fe^{2+}][H_3PO_4] - 0.1775\ pH$
6	$Fe_3(PO_4)_2 \cdot nH_2O + 6H^+ = 3Fe^{2+} + 2H_3PO_4 + nH_2O$	$pH = 0.3654 - 1/3\ lg\ [H_3PO_4] - 1/2\ lg\ [Fe^{2+}]$
7	$3FePO_4 \cdot 2H_2O + 3e + 3H^+ = Fe_3(PO_4)_2 \cdot nH_2O + H_3PO_4 + (6-n)$ H2O	$E = 0.1083 - 0.0197\ lg\ [H_3PO_4] - 0.0592\ pH$
8	$3LiFePO_4 + nH_2O + 3H^+ = Fe_3(PO_4)_2 \cdot nH_2O + 3Li^+ + H_3PO_4$	$pH = 1.1112 - lg\ [Li^+] - 1/3\ lg\ [H_3PO_4]$
9	$LiFePO_4 + 3H^+ = Fe^{2+} + Li^+ + H_3PO_4$	$pH = 0.6137 - 1/3\ lg\ [Li^+][Fe^{2+}][H_3PO_4]$
10	$FePO_4 \cdot 2H_2O + Li^+ + e = LiFePO_4 + 2H_2O$	$E = 0.0426 + 0.0592\ lg\ [Li^+]$
11	$Li_3PO_4 + Fe(OH)_3 + 3H^+ = FePO_4 \cdot 2H_2O + 3Li^+ + H_2O$	$pH = 6.0831 - lg\ [Li^+]$

12	$Fe(OH)_3 + Li_3PO_4 + 3H^+ + e = LiFePO_4 + 2Li^+ + 3H_2O$	$E = 1.1224 - 0.1183 \lg [Li^+] - 0.1775 pH$
13	$Fe(OH)_2 + Li_3PO_4 + 2H^+ = LiFePO_4 + 2H_2O + 2Li^+$	$pH = 7.4167 - \lg [Li^+]$
14	$Fe(OH)_3 + H^+ + e = Fe(OH)_2 + H_2O$	$E = 0.2447 - 0.0592 pH$

Table S4. Standard electrode potential for some electrical couples in the aqueous solution

Electrode reaction	E^0/V
$S_2O_8^{2-}+2e=2SO_4^{2-}$	$E^0=2.010V$
$H_2O_2+2H^+=2H_2O$	$E^0=1.770V$
$Fe^{3+}+e=Fe^{2+}$	$E^0=0.7696V$
$O_3+2H^++2e=O_2+H_2O$	$E^0=2.07V$
$O_2+4H^++4e=2H_2O$	$E^0=1.229V$
$O_2(air)+4H^++4e=2H_2O$	$E^0=1.218V$

where E^0 is the standard electrode potentials of the corresponding half-reactions for these oxidants at 298.15 *K*.

3.2 Leaching behavior in the air oxidation water leaching process

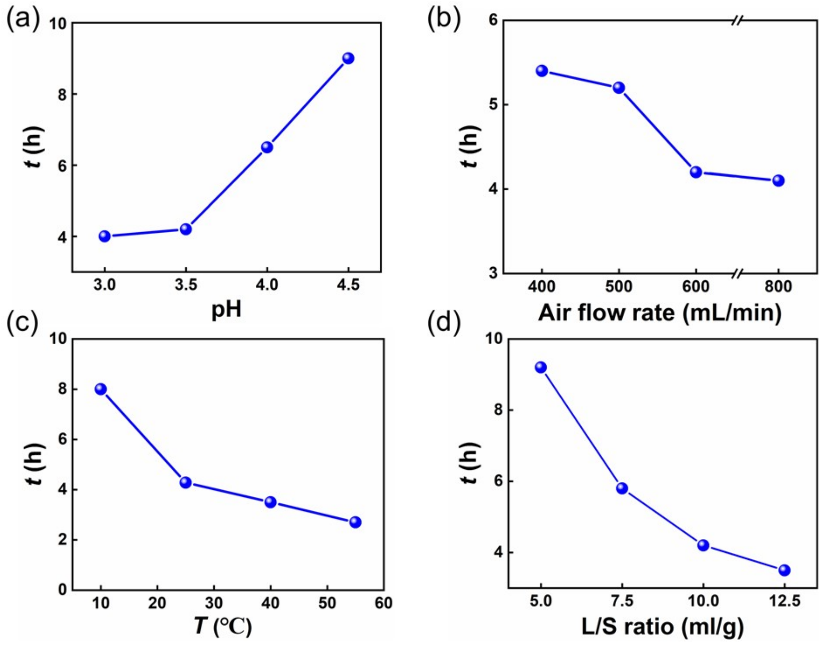

Fig. S2 the required *t* of 95% dilithiated from spent LFP under different conditions.

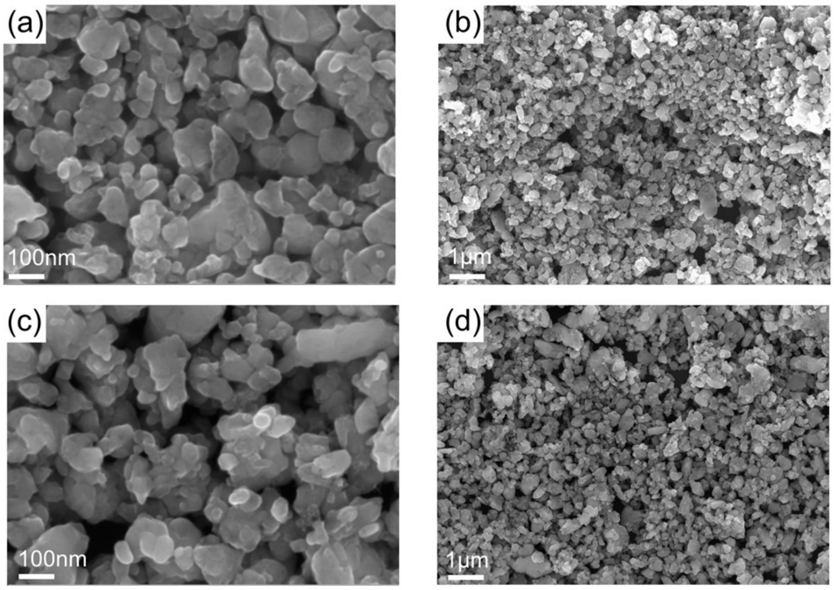

Fig. S3. SEM images of the (a, b) spent LFP cathode material, (c, d) leaching residue under different enlargement factors.

3.3 Lithium leaching kinetics

Table S5. Parameters of the Avrami model for air oxidation-water leaching of Li at different pH value

pH	*n*	*k* (h^{-1})	R^2
3.0	1.09544	0.6107	0.9933
3.5	1.02133	0.4232	0.9854
4.0	0.95623	0.2922	0.9920
4.5	0.89211	0.3054	0.9918

Table S6. Parameters of the Avrami model for air oxidation-water leaching of Li at different air flow rate

Air flow rate (ml/min)	*n*	*k* (h^{-1})	R^2
400	0.9927	0.3215	0.992
500	1.04797	0.3476	0.9876
600	0.91531	0.4232	0.9938
800	0.86922	0.4712	0.9921

Table S7. Parameters of the Avrami model for air oxidation-water leaching of Li at different L/S ratio

L/S (mL/g)	*n*	*k* (h^{-1})	R^2
5	0.83536	0.2411	0.9922
7.5	0.88572	0.3195	0.9805
10	0.9151	0.4263	0.9919
12.5	1.10317	0.6882	0.9917

Table S8. Parameters of the Avrami model for air oxidation-water leaching of Li at different temperatures

Temperature (°C)	*n*	*k* (h^{-1})	R^2

10	1.04462	0.2946	0.9857
25	1.02133	0.4232	0.9935
40	1.11489	0.5756	0.9900
55	1.15709	0.7643	0.9900

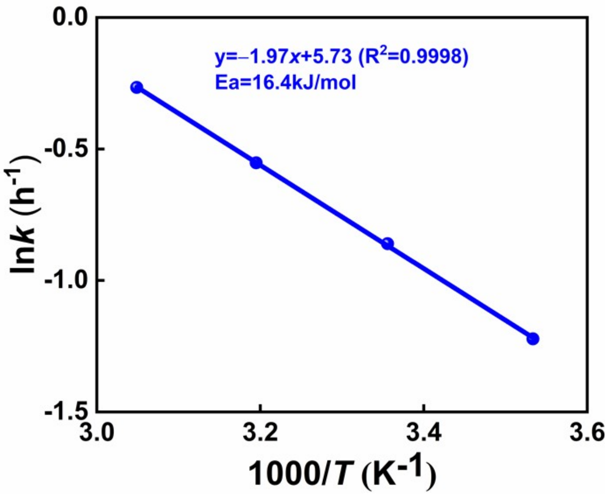

Figure S4. Arrhenius plot for the air oxidation leaching of Li from 10 °C to 55 °C

3.5 Regeneration of LFP cathode material

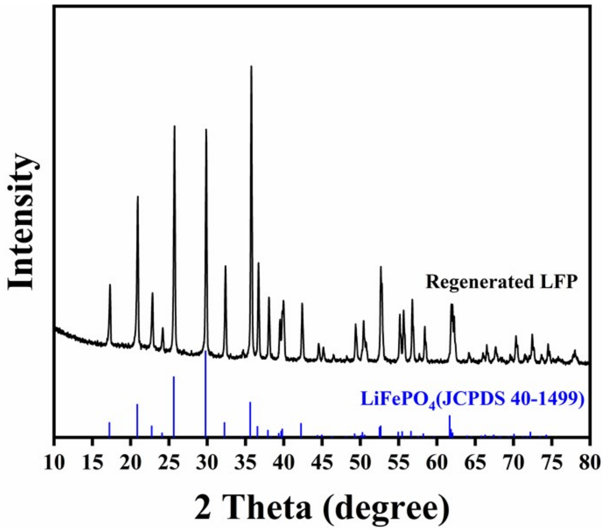

Fig. S5 XRD pattern of the regenerated LFP material

3.6 Preliminary analysis of the proposed technology

A preliminary economic analysis was carried out to evaluate the benefits of recycling 1 ton spent LFP cathode powders. The spent cathode material contains 4.47% of Li by weight and the recovery rate of Li is 98%. Procedures mainly included leaching, filtering, drying, evaporative crystallization and freeze crystallization. The price of various products, reagents and the expenditure, including energy, water, labor, equipment depreciation and maintenance were from the latest data of the Internet and some available literatures[8, 11]. The average wage per labor is $14366.7 per year in China and assumed the working day is 300 days and 8 h of the working time. The results of the calculation are shown in **table S9**.

Revenue：The products in this process are Li_2CO_3, $FePO_4$, $Na_2SO_4 \cdot 10H_2O$, the price is 13.83[1], 0.84[2], 0.05[3] $\$ \cdot kg^{-1}$, respectively. The total revenue from 1 ton spent LFP cathode powders is calculated as the following formula:

$$R = P_i \times m_i = \$13.8 \times 233.6 + \$0.84 \times 960 + \$0.05 \times 1022.70 = \$4081.2$$

where R, P_i and m_i represent revenue, price of the product of i and mass of product of i.

Costs of reagents: The dosage of H_2SO_4, Na_2CO_3, are 322.05 and 358.44 kg, and the price is 0.215 and 0.3 $\$ \cdot kg^{-1}$. The total cost of reagents is calculated as followed:

$$C_r = p_i \times m_i = \$0.125 \times 322.1 + \$0.19 \times 358.4 = \$108.4$$

C_r, p_i and m_i are the cost of reagents, price of reagent i and mass of reagent i.

The costs of electricity and water: The total energy consumption of all procedures is 1706 kWh. Water consumption of all procedures is 7 tons. The prices are 0.19 $\$ \cdot kWh^{-1}$ and 0.91 $\$ \cdot ton^{-1}$:

$$C = C_E + C_W = p_e \times E_p + p_w \times m_w = \$0.19 \times 1706 + \$0.91 \times 7 = \$330.5$$

where C_W represents the cost of water consumption, C_E represents the cost of the total consumption of the whole procedure. p_e p_w E_p m_w are the price of energy, price of water, energy consumption of all procedures and mass of water, respectively.

The cost of labor: The actual industrial production can recycle 10 tons of spent cathode powders per day. So, the cost of labor to recycle 1ton cathode powders can be calculated as followed:

$$C_l = n \times W_l/10 = 24 \times 47.89 \div 10 = \$114.9$$

where C_l represents the cost of labor; n represents the number of workers; W_l represents the wage per labor.

Table S9 Economic analysis for recycling 1 ton of spent LFP cathode material by the proposed method in China (exchange rate: 1 \$ = 6.4 CNY)

Revenue	Product benefits			
	Products	Price ($\$\cdot kg^{-1}$)	Mass(kg)	Profit ($)
	Li_2CO_3	13.8[1]	233.6	3223.7
	$FePO_4$	0.84[2]	960.0	806.4
	$Na_2SO_4\cdot 10H_2O$	0.05[3]	1022.7	51.1
	Total			4081.2
Cost	Reagents Cost			
	Reagent	Price ($\$\cdot kg^{-1}$)	Mass(kg)	Cost ($)
	Spent LFP cathode material		1000	1406.3

	H_2SO_4	0.125[4]	322.1	-40.3
	Na_2CO_3	0.19[5]	358.4	-68.1
Cost	Energy Cost			
	Procedure	Energy consumption(kWh)	Price ($\$\cdot kWh^{-1}$)	Cost ($)
	Leaching	200	0.19[8]	-38
	Filtering, drying	230	0.19	−43.7
	Evaporative crystallization	1100	0.19	−209
	Freeze crystallization	176	0.19	−33.4
	Other Cost			Cost ($)
	Water	Consumption(ton)	Price ($\$\cdot ton^{-1}$)	
		7	0.91[6]	-6.4
	Labor			-114.9[7]
	Depreciation of equipment			-76[8]
	Maintenance of equipment			-15[11]
Profits ($)				2030.1

Table S10. Summary of different processes for the selective extraction of Li from LFP material

Cathode material	Methods	Acid	Oxidant	Recovery efficiency	Ref.

$LiFePO_4$	Direct oxidation		$Fe_2(SO_4)_3$+H_2O_2	96.5% Li	[9]
$LiFePO_4$	Direct oxidation		$Na_2S_2O_8$	99% Li	[8]
$LiFePO_4$	Direct oxidation	H_2SO_4	H_2O_2	96.9% Li	[10]
$LiFePO_4$	Direct oxidation	CH_3COOH	H_2O_2	95.1% Li	[11]
$LiFePO_4$	Direct oxidation	H_2SO_4	H_2O_2	94.9% Li	[12]
$LiFePO_4$	Direct oxidation	Citric acid	H_2O_2	94.9% Li	[13]
$LiFePO_4$	High-temperature conversion	H_2SO_4		98.5% Li	[14]
$LiFePO_4$	Mechanochemical activation			96.3% Li	[15]
$LiFePO_4$	Mechanochemical activation		$Na_2S_2O_8$	99.7% Li	[16]
$LiFePO_4$	Electrolysis		$K_3Fe (CN)_6$	99.8% Li	[17]
$LiFePO_4$	Electrolysis			98% Li	[18]
$LiFePO_4$	Electrolysis			95.2% Li	[19]
$LiFePO_4$	Direct oxidation	H_2SO_4	Air	99.3% Li	This work

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