Electronic Supplementary Material (ESI) for Green Chemistry.
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Electronic Supplementary Information (ESI) for:

Selective Recovery of Lithium from Cathode Scrap of Spent Lithium Iron Phosphate Batteries: A Green Sustainably Process

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Eight types of leaching solutions:

Solution 1: 0.8mol·L^{-1} oxalic acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 2: 0.8mol·L^{-1} citric acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 3: 0.8mol·L^{-1} acetic acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 4: 0.8mol·L^{-1} acetic acid at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 5: H_2O with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 6: 0.8mol·L^{-1} hydrochloric acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 7: 0.4mol·L^{-1} sulfuric acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Solution 8: 0.8mol·L^{-1} nitric acid with 6 vol.% H_2O_2 at 50°C for 1h, the solid to liquid ratio is 100g·L^{-1}.

Table S1. Experimental Results of the Orthogonal Design

No.	Influencing factor					Leaching efficiency（%）
	Reaction temperature (ºC)	Time (min)	Acid concentration (mol/L)	H_2O_2 content (vol.%)	S/L ratio (g/L)	Li
1	25	30	0.2	2	100	22.09
2	25	40	0.4	4	120	87.71
3	25	50	0.6	6	140	86.59
4	25	60	0.8	8	160	91.18
5	40	30	0.4	6	160	87.98
6	40	40	0.2	8	140	55.72
7	40	50	0.8	2	120	61.21
8	40	60	0.6	4	100	91.66

9	50	30	0.6	8	120	93.74
10	50	40	0.8	6	100	94.54
11	50	50	0.2	4	160	49.41
12	50	60	0.4	2	140	75.41
13	60	30	0.8	4	140	85.10
14	60	40	0.6	2	160	46.39
15	60	50	0.4	8	100	85.15
16	60	60	0.2	6	120	49.17

Table S2. Analysis Results of Orthogonal Experiments for Li

Effect factor	Temperature	Time	Acid	H_2O_2	S/L ratio
K1	71.89	72.23	44.10	51.28	58.69
K2	74.14	71.09	84.06	78.47	72.96
K3	78.27	70.59	79.60	79.57	75.71
K4	66.45	76.86	83.00	81.45	68.74
Extreme deviation	11.75	6.27	38.90	30.17	17.02

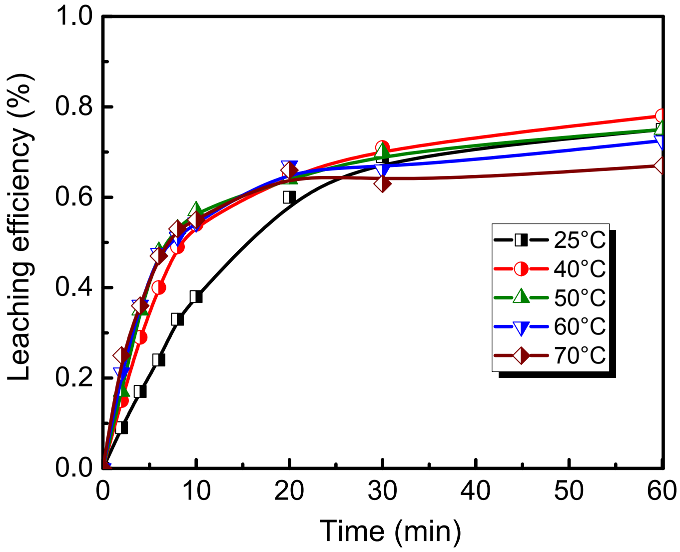


Figure S1. Leaching efficiency of Fe from the spent $LiFePO_4$ under different leaching time ($0.8 mol \cdot L^{-1}$ CH_3COOH, S/L ratio of 120 $g \cdot L^{-1}$, 6 vol.% H_2O_2)

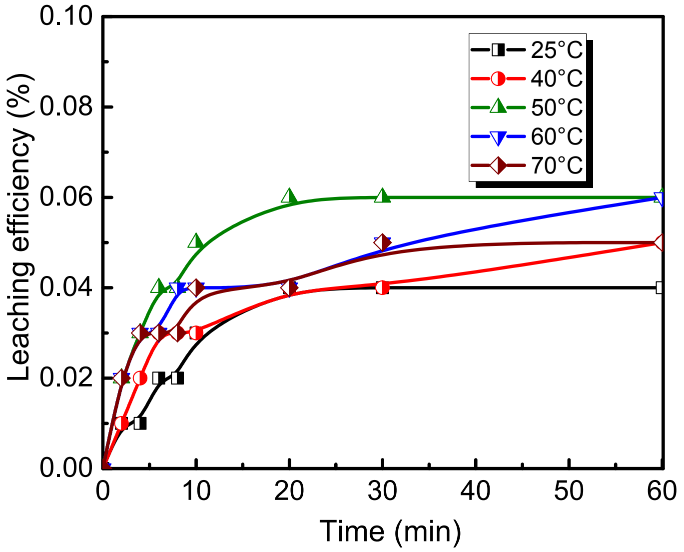
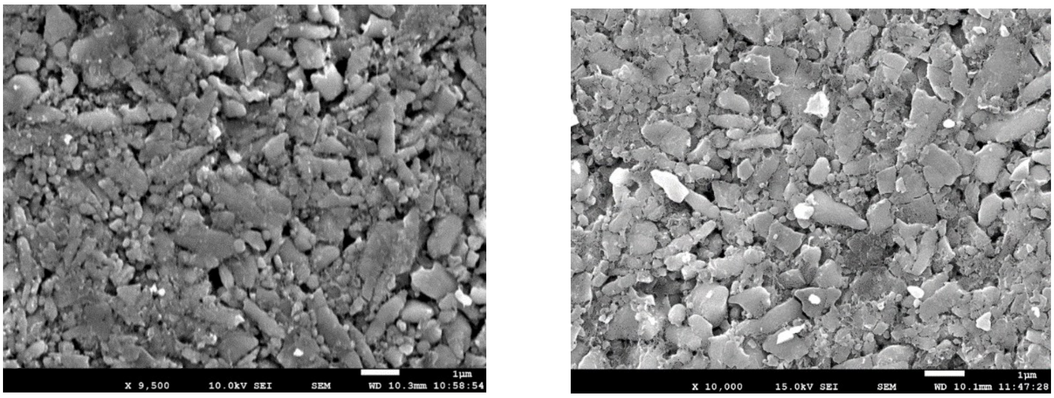
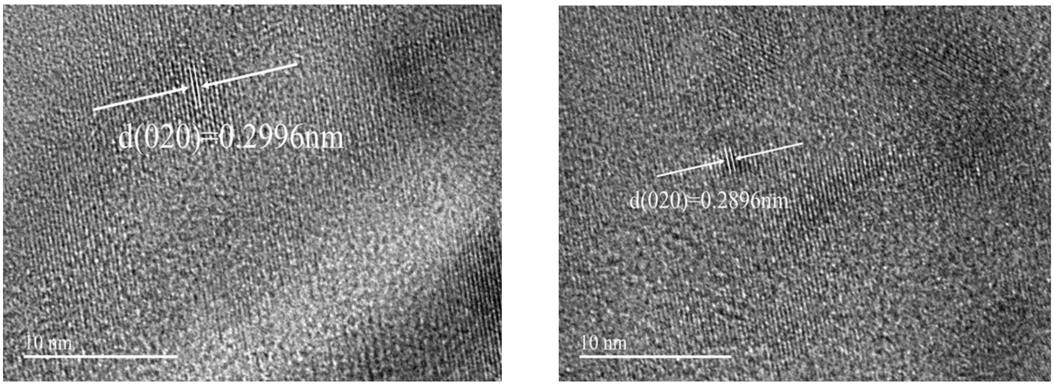


Figure S2. Leaching efficiency of Al from the spent $LiFePO_4$ under different leaching time ($0.8 mol \cdot L^{-1}$ CH_3COOH, S/L ratio of $120\ g \cdot L^{-1}$, 6 vol.% H_2O_2)



(a) (b)

Figure S3 Scanning electron microscope (SEM) images of solid samples (a) raw LiFePO4 cathode scrap; (b) final product



(a) (b)

Figure S4 TEM images of solid samples (a) raw LiFePO4 cathode scrap; (b) final product

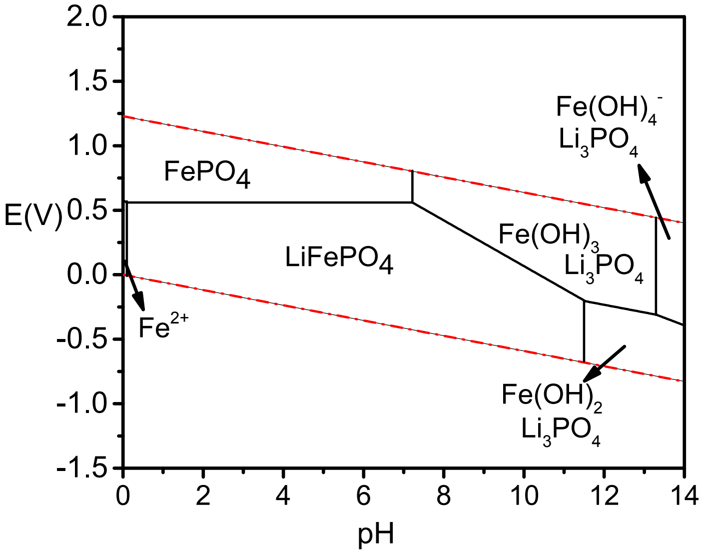
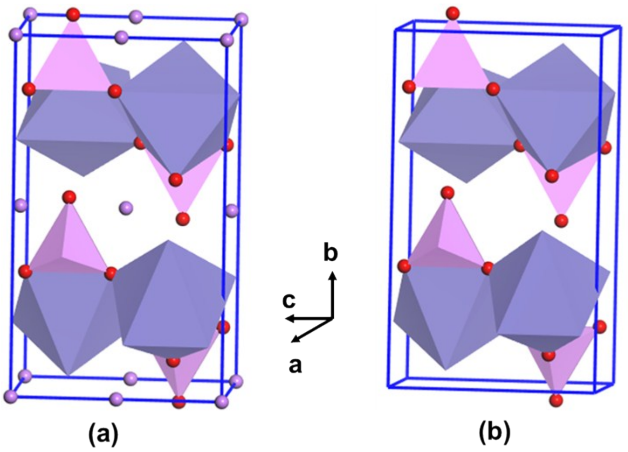


Figure S5. E-pH diagram of Li-Fe-P-H2O system ([Li]=[Fe]=[P]=1mol/L)[1]



(a) (b)

Figure S6. Crystal structure of (a) $LiFePO_4$ and (b) $FePO_4$

Table S3. The space group and lattice parameters of $LiFePO_4$ and delithiated phase $FePO_4$

	$LiFePO_4$	$FePO_4$
Space Group	P n m a	P n m a
a (Å)	10.334 (1)	9.814 (1)
b (Å)	6.010 (1)	5.789 (1)
c (Å)	4.693 (1)	4.782 (1)

Volume (Å3)	291.47 (1)	271.68 (1)

Generally, for a chemical reaction: Aa + Bb +… = cC + dD +… The change of Gibbs energy for the reaction is expressed as eq. (S1):

$$\Delta G_{\mathrm{r}} = \sum v_i G_i(\text{products}) - \sum v_i G_i(\text{reactants}) = (cG_C + dG_D + ...) - (aG_A + bG_B + ...) \qquad \text{(S1)}$$

Table S4. Thermodynamic data of relevant chemical reactions during leaching

Substance	$\Delta_f G_m^{\theta}$(kJ·mol^{-1})	references
H^+(aq)	0	2
Li^+(aq)	-293.31	
CH_3COO^-(aq)	-369.31	
CH_3COOH(l)	-389.9	
H_2O_2(l)	-120.35	
H_2O(l)	-237.129	
$FePO_4$(s)	−1110.14	3
$LiFePO_4$ (s)	−1480.97	

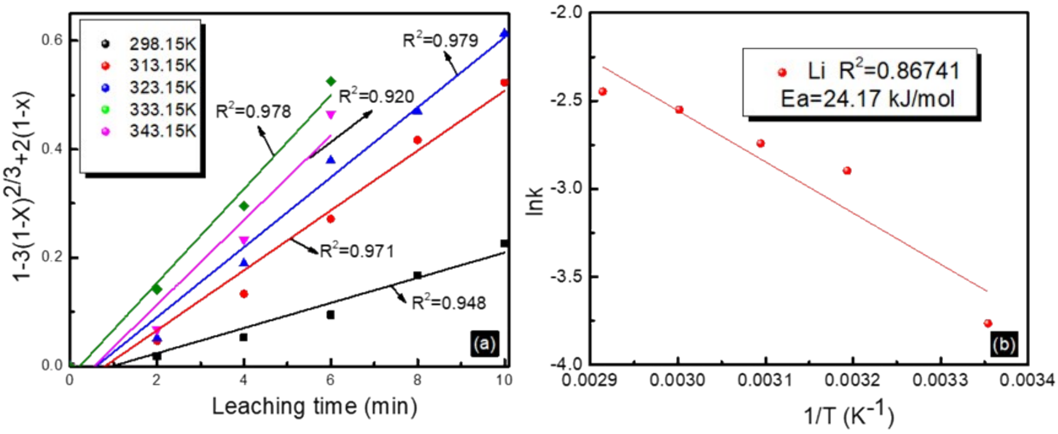


Figure S7. Plots of 1– (1–X)$^{2/3}$+2(1-X) vs. t under different reaction temperatures for Li (a). Arrhenius plots for leaching of Li from the cathode scrap calculated by the surface chemical reaction model (b)

Table S5 Purity analysis of the final product for Li_2CO_3 under the optimized process

Content	$LiCO_3$	Al	Fe	Na	PO_4^{3-}
Composition (wt.%)	99.95(79)	0.0043	0.0016	0.0247	0.0115

Table S6 Some principles of green chemistry applied to recover metals[4]

Prevention	It is better to prevent waste than to treat or clean up waste after it is formed
Atom Economy	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product
Safer solvents and Auxiliaries	Use of auxiliary substances (e.g., solvents separation agents, etc.) should be made unnecessary, whenever possible and, when used, innocuous
Use of renewable feed stocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable
Design for energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized
Inherently safer chemistry	Substance and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires

Table S7 Purity analysis of the final product for aluminum foil under the optimized process

Content	Al	Fe_2O_3	Li_2O	PO_4^{3-}
Composition (wt.%)	99.23(04)	0.4223	0.0090	0.3383

Table S8 Purity analysis of the final product for $FePO_4$ under the optimized process

Content	$FePO_4$	Al	Fe	Li	P
Composition (wt.%)	99.68(57)	0.0993	33.50(95)	0.2151	19.46(02)

Re-synthesis of $LiFePO_4$/C samples

$LiFePO_4$/C samples were synthesized via a carbothermal reduction method using recycled $FePO_4$ and Li_2CO_3 as raw materials. For a typical synthesis, the mixture of $FePO_4$ and Li_2CO_3 in a molar ratio of 1:1.05, and glucose in a 20:100 weight ratio to $LiFePO_4$ product were first ball-milled together for 7 h with ethanol as a dispersant. The obtained mixture was heated to 300 ºC under an argon atmosphere for 4 h. The mixture was then ground and heated to 700ºC under an argon atmosphere for 10 h. The product (*i.e.* $LiFePO_4$/C) was ground in an agate mortar for later use.

Electrochemical tests

Electrochemical tests were carried out by using CR2025-type coin cells at room temperature. The re-synthesized $LiFePO_4$/C was mixed with acetylene black and PVDF in a weight ratio of 80:10:10 in NMP. Coin cells used lithium foil as anode and 1.0 mol/L LiPF6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) in the volume ratio of 1:1 as electrolyte. Meantime, these cells were assembled in the argon-filled glove box with both moisture and oxygen content below 0.1 ppm. Galvanostatic cycling tests were performed on a LAND CT2001A battery tester with the voltage between 2.5 and 4.3V (versus Li+/Li) at the current density of 0.1C (1C=170mA $g^{-1)}$. Rate performance was carried out at the current density of 0.1C, 0.2C, 0.5C, 1C, 2C, 5C.

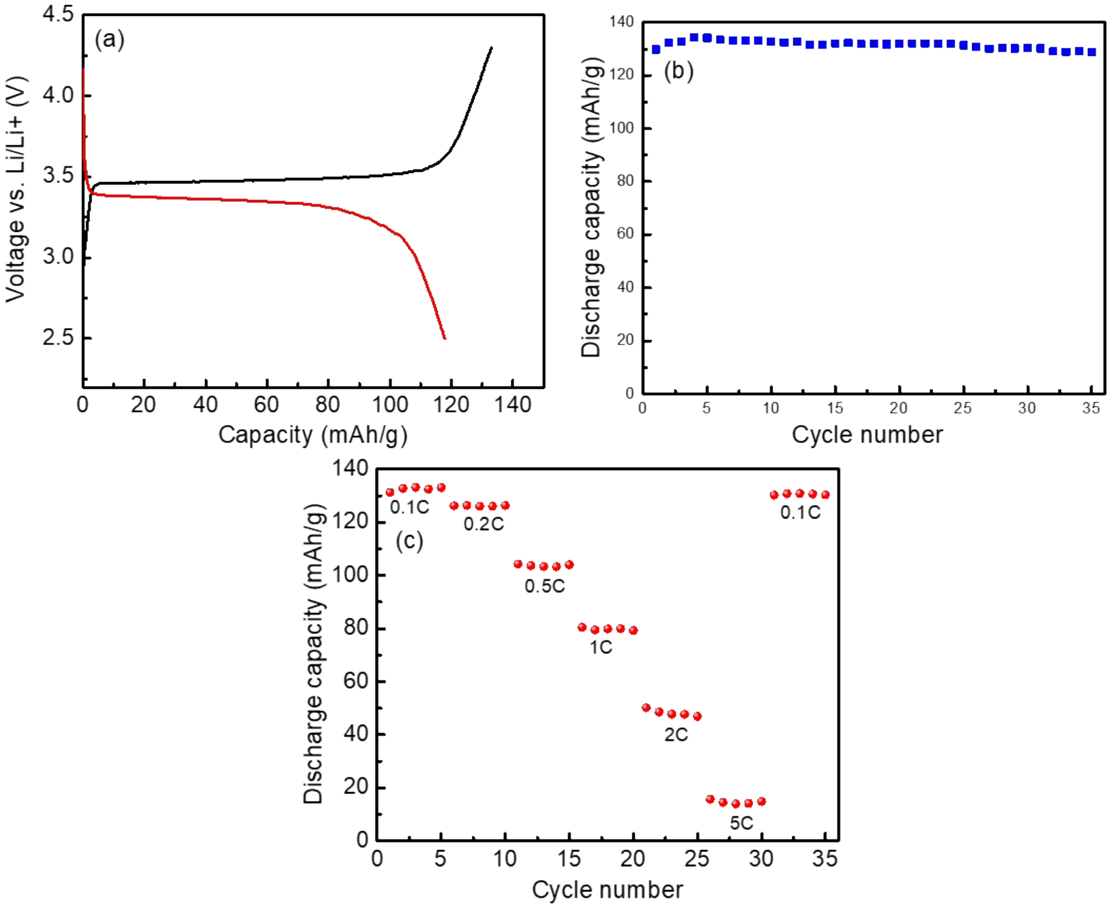


Figure S8. Electrochemical performances of regenerated $LiFePO_4$ cathode material at 25°C between 2.5 V and 4.3 V: (a) 0.1 C, (b) cycling performance, (c) rate capability.

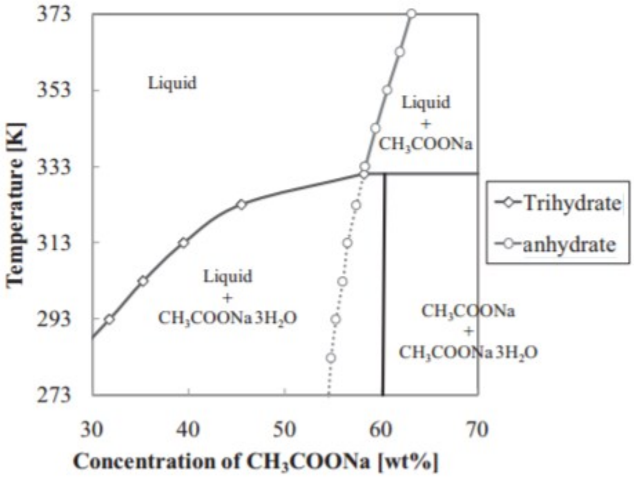


Figure S9. Phase diagram of the CH3COONa-water system[5]

Economic and energy consumption prospective of the integrated process

The recycling process in this study can be divided into five parts: NaCl-Discharging and

Dismantling; Leaching; Filtering, Drying and Sieving; Purification; Precipitation. It was assumed that 1 ton of spent $LiFePO_4$ batteries (18650) were treated by our **green recycling** process in China. The assumption of the cost of labour: the working day is 300 days per year (average 25 days per month) and the working time is about 8 hours every day. The average wage of per labor is 74318 CNY per year[6] (\$39 per day, 1\$=6.367 CNY) in china. The assumption of the costs of electricity charge and water price: the industrial electricity charge is \$0.20/kWh (maximum=1.3 CNY, 1\$=6.367 CNY)[7], and the industrial water charge is \$0.91/t (maximum)[8].

Considering the residuals rate and interest rate, depreciation cost of equipment is calculated as Eq. (S2) while the cost of equipment maintenance cost is calculated as Eq. (S3):

$$C_D = C_o \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} \tag{S2}$$

C_D ——— Depreciation cost of equipment

C_O ——— Acquisition cost of equipment

r ——— Residuals rate of equipment, 4%

i ——— Interest rate, 10%

n ——— Service life, year

$$M_c = 0.05 \times C_o \tag{S3}$$

M_C ——— Maintenance cost of equipment

C_O ——— Acquisition cost of equipment

And the energy consumption, the cost of energy, water and labor are calculated as Eq. (S4), (S5), (S6) and (S7):

$$E_P = P \times t \tag{S4}$$

E_p ——— Energy consumption of the process

P ——— Equipment power, Kw

t ——— Working time of equipment

$$C_P = E_P \times p_e \tag{S5}$$

C_p ——— Cost of energy

E_p ——— Energy consumption of the process

p_e ——— Electricity price for industrial uses,\$0.20/kWh

$$C_W=m\times p_w \tag{S6}$$

C_w ——— Cost of water

m ——— Water consumption, ton

p_w ——— Water price for industrial uses, \$0.91/t

$$C_l=n\times p_l \tag{S7}$$

C_l ——— Cost of labor

n ——— number of workers

p_l ——— Wage of per labor, \$39/day

Finally, the energy consumption and the cost of every process and revenue of products in this study were calculated in detailed and then a profit was obtained by recycling 1 ton spent $LiFePO_4$ batteries with the current process as follows in China.

Process I: NaCl-discharging and dismantling:

NaCl-discharging requirement: discharging in 5wt.% NaCl solution for 12 h, batteries/solution = 1:10 w/w (assume that the discharging is done at the night before); about 0.5 ton of NaCl and 10 ton of water were needed in the discharging process; one person, a set of automatic conveyor belts (P=7.5kW, per price= \$2000, 2.0 m/s, maximum capacity=1000 m^3 /h, service life=5 years) work for 1 hour every day.

$$C_D=C_o\times(1-r)\times\frac{i}{1-(1+i)^{-n}}=(\$2000\times\frac{1}{300})\times(1-4\%)\times\frac{10\%}{1-(1+10\%)^{-5}}=\$1.69$$

$$M_c=0.05\times C_o=0.05\times(\$2000\times\frac{1}{300})=\$0.33$$

$$E_P=P\times t=7.5kW\times 1h=7.5kW\times h$$

$$C_P=E_P\times p_e=7.5kW\times h\times \$0.2/kWh=\$1.5$$

$$C_l=n\times p_l=1\times \$39=\$39$$

Dismantling: There is no commercial automatic dismantling equipment on the market, a small automated dismantling device was designed for spent $LiFePO_4$ batteries. The dismantling device as shown in **Figure S10.** (P=2kW, maximum capacity=10kg/h, work time=100h)

$$E_P = P \times t = 2kW \times 100h = 200kW \times h$$

$$C_P = E_P \times p_e = 200kW \times h \times \$0.2/kWh = \$40$$

Compared with mechanical dismantling, the cost of manual dismantling is also calculated. (manual dismantling maximum capacity=5kg/h, work time=200h, number of workers=25)

$$C_l = n \times p_l = 25 \times \$39 = \$975$$

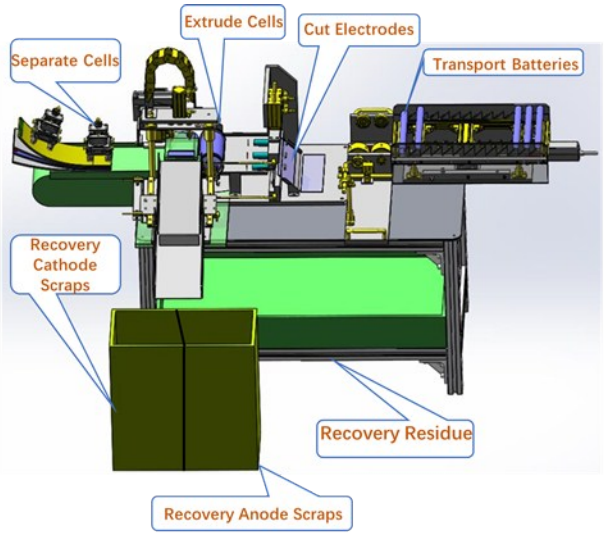


Figure S10. Schematic plot of the dismantling device

The NaCl solution can be used repeatedly, where their costs are not included in the total cost of discharge. The dismantling costs were calculated using laboratory-made dismantling equipment.

Energy consumption: 207.5kW·h;

Cost of energy: $41.5;

Cost of process: $41.02;

Total costs: $82.52.

After this process, about 330kg spent $LiFePO_4$ cathode scraps can be obtained in this study.

Process Ⅱ: Leaching

Requirement: One set of glass lining reactor (Internal Electric Heater) (P=45Kw, per price=$3955, maximum capacity = 1000L/per, service life = 5 years) was used to leaching reaction. In this process, the obtained spent $LiFePO_4$ cathode scraps were treated in batches of 3 by the reactor, which means the device needs to work 3 times every day. About 110 kg was reacted in every device every time.

The working time including temperature rise and hold is 1.5 hour every time. About 5ton water was consumed.

$$C_D = C_0 \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} = (\$3955 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$3.34$$

$$M_c = 0.05 \times C_o = 0.05 \times (\$3955 \times \frac{1}{300}) = \$0.66$$

$$E_P = P \times t = 45kW \times 1.5h \times 3 = 202.5kW \times h$$

$$C_P = E_P \times p_e = 202.5kW \times h \times \$0.2 / kWh = \$40.5$$

$$C_W = m \times p_w = 5t \times \$0.91 / t = \$4.55$$

$$C_l = n \times p_l = 1 \times \$39 = \$39$$

Energy consumption: 202.5kW·h;

Cost of energy: \$40.5;

Cost of process: \$47.55;

Total costs: \$88.05.

Process Ⅲ Filtering, Drying and Sieving

Filtering requirement: A set of frame filter (P=10Kw, per price=\$8350, maximum capacity = 30m^2/per, service life = 5 years) is needed to work for 2 h. About 2 ton of water is consumed.

$$C_D = C_0 \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} = (\$8530 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$7.05$$

$$M_c = 0.05 \times C_o = 0.05 \times (\$8530 \times \frac{1}{300}) = \$1.42$$

$$E_P = P \times t = 10kW \times 2h = 20kW \times h$$

$$C_P = E_P \times p_e = 20kW \times h \times \$0.2 / kWh = \$4$$

$$C_W = m \times p_w = 2t \times \$0.91 / t = \$1.82$$

$$C_l = n \times p_l = 1 \times \$39 = \$39$$

Drying requirement: A conveyor drier (P=40Kw, per price=\$15180, maximum capacity = 200kg/per, service life = 5 years) is needed to work for 4h.

$$C_D = C_0 \cdot (1-r) \cdot \frac{i}{1-(1+i)^{-n}} = (\$15180 \times \frac{1}{300}) \times (1-4\%) \times \frac{10\%}{1-(1+10\%)^{-5}} = \$12.81$$

$$M_c = 0.05 \cdot C_o = 0.05 \times (\$15180 \times \frac{1}{300}) = \$2.53$$

$$E_P = P \cdot t = 45kW \times 4h = 180kW \cdot h$$

$$C_P = E_P \cdot p_e = 180kW \cdot h \times \$0.2 / kWh = \$36$$

$$C_l = n \cdot p_l = 1 \times \$39 = \$39$$

Sieving requirement: A set of vibration screener (Pw=15Kw, per price=$1260, maximum capacity = 200kg/h, service life = 5 years) is needed to work for 2 h.

$$C_D = C_0 \cdot (1-r) \cdot \frac{i}{1-(1+i)^{-n}} = (\$1260 \times \frac{1}{300}) \times (1-4\%) \times \frac{10\%}{1-(1+10\%)^{-5}} = \$1.06$$

$$M_c = 0.05 \cdot C_o = 0.05 \times (\$1260 \times \frac{1}{300}) = \$0.21$$

$$E_P = P \cdot t = 15kW \times 2h = 30kW \cdot h$$

$$C_P = E_P \cdot p_e = 30kW \cdot h \times \$0.2 / kWh = \$6$$

$$C_l = n \cdot p_l = 1 \times \$39 = \$39$$

Energy consumption: 230 kW·h;

Cost of energy: $46;

Cost of process: $143.9;

Total costs: $189.9.

Process Ⅴ: Purification

Leaching liquid is mechanically evaporated, which is achieved by two multiple-stage evaporators (P = 40 kW, per price = $36000, maximum capacity = 1ton/hour, service life = 5 years), while the second one is naturally evaporated.

$$C_D = C_0 \cdot (1-r) \cdot \frac{i}{1-(1+i)^{-n}} = (\$36000 \times \frac{1}{300}) \times (1-4\%) \times \frac{10\%}{1-(1+10\%)^{-5}} = \$30.38$$

$$M_c = 0.05 \cdot C_o = 0.05 \times (\$36000 \times \frac{1}{300}) = \$6$$

$$E_P = P \cdot t = 40kW \times 3h = 120kW \cdot h$$

$$C_P = E_P \cdot p_e = 120kW \cdot h \times \$0.2 / kWh = \$24$$

$$C_l = n \times p_l = 1 \times \$39 = \$39$$

Energy consumption: 120 kW·h;

Cost of energy: \$24;

Cost of process: \$75.38;

Total costs: \$99.38.

Process Ⅵ: Precipitation

Requirement: two set of glass lining reactors (Internal Electric Heater) (P=25Kw, per price=\$1955, maximum capacity =500L/per, service life = 5 years) are needed to respectively work for 4h including temperature rise and hold. About 4ton water was consumed.

$$C_D = C_o \times (1 - r) \times \frac{i}{1 - (1 + i)^{-n}} = (\$1955 \times \frac{1}{300}) \times (1 - 4\%) \times \frac{10\%}{1 - (1 + 10\%)^{-5}} = \$1.65$$

$$M_c = 0.05 \times C_o = 0.05 \times (\$1955 \times \frac{1}{300}) = \$0.33$$

$$E_P = P \times t = 25kW \times 4h = 100kW \times h$$

$$C_P = E_P \times p_e = 100kW \times h \times \$0.2 / kWh = \$20$$

$$C_W = m \times p_w = 4t \times \$0.91 / t = \$3.64$$

$$C_l = n \times p_l = 1 \times \$39 = \$39$$

Energy consumption: 100 kW·h;

Cost of energy: \$20;

Cost of process: \$44.62;

Total costs: \$64.62.

Therefore, the whole energy consumption (E_T) and the total cost of energy (C_E) the cost of the process (C_c) and the total costs of whole processes (C_T) in this study can be calculated:

$$E_T = 207.5\ \text{kW·h} + 202.5\ \text{kW·h} + 230\ \text{kW·h} + 120\ \text{kW·h} + 100\ \text{kW·h} = 860\ \text{kW·h}$$

$$C_E = \$41.5 + \$40.5 + \$46 + \$24 + \$20 = \$172$$

$$C_c = \$41.02 + \$47.55 + \$143.9 + \$75.38 + \$44.62 = \$352.47$$

$$C_T = \$82.52 + \$88.05 + \$189.9 + \$99.38 + \$64.62 = \$524.47$$

From the perspective of reagent cost and product value, the economic prospective of the integrated process is given in **Table 5,** the revenue can be calculated:

P_r**=$1069.2+$260.7+$115.36-$0.70-$19.24-$180.36-$73.92=$1171.04**

Thus, the total processing revenue (P) can be obtained by treating 1ton spent $LiFePO_4$ batteries with current green recycling process:

$P=P_r-C_T$**=$1171.04-$524.47=$646.57**

In summary, when dealing with 1ton spent $LiFePO_4$ batteries, the total profit of whole processes (C_T), the whole energy consumption (E_T) and the total cost of energy (C_E) in this study are ***$646.57, 860*****kW·h and *****$172.***

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