Electronic Supplementary Information (ESI)

Direct Recovery of Scraped $LiFePO_4$ by a Green and Low-Cost Electrochemical Re-lithiation Method

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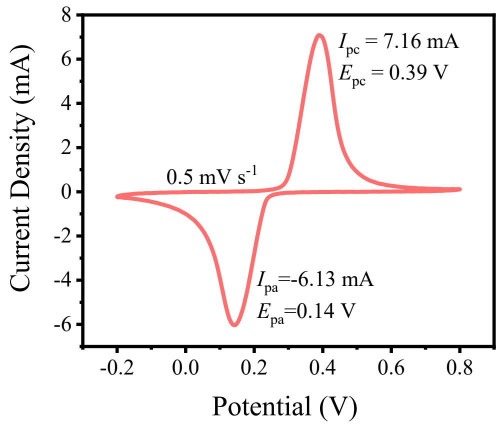

Fig. S1 CV curve of S-LFP in lithium sulfate aqueous solution.

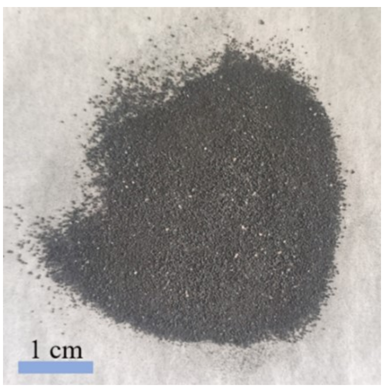

Fig. S2 S-LFP cathode powder stemming from retired LFP battery.

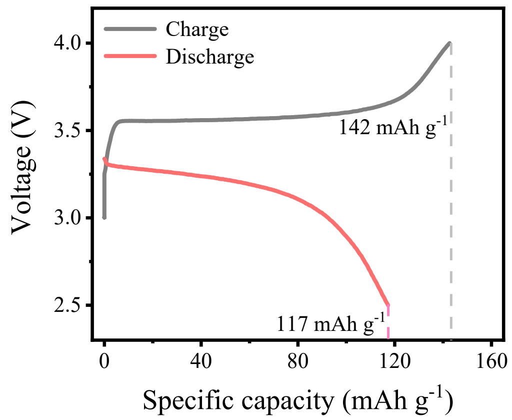

Fig. S3 The first charge/discharge profiles of S-LFP at 1 C (1 C = 170 mAh g^{-1}).

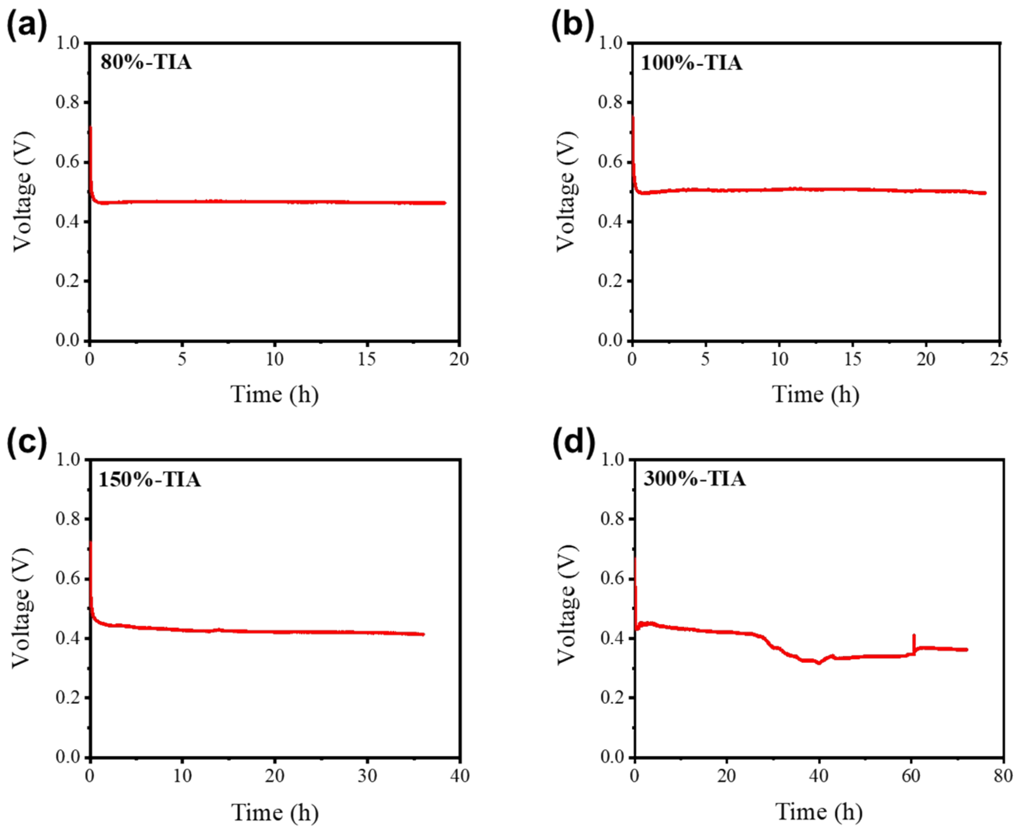

Fig. S4 The Discharge curves of re-lithiation process at different TIA. (a) 80%-TIA, (b) 100%-TIA, (c)150%-TIA, and (d) 300%-TIA.

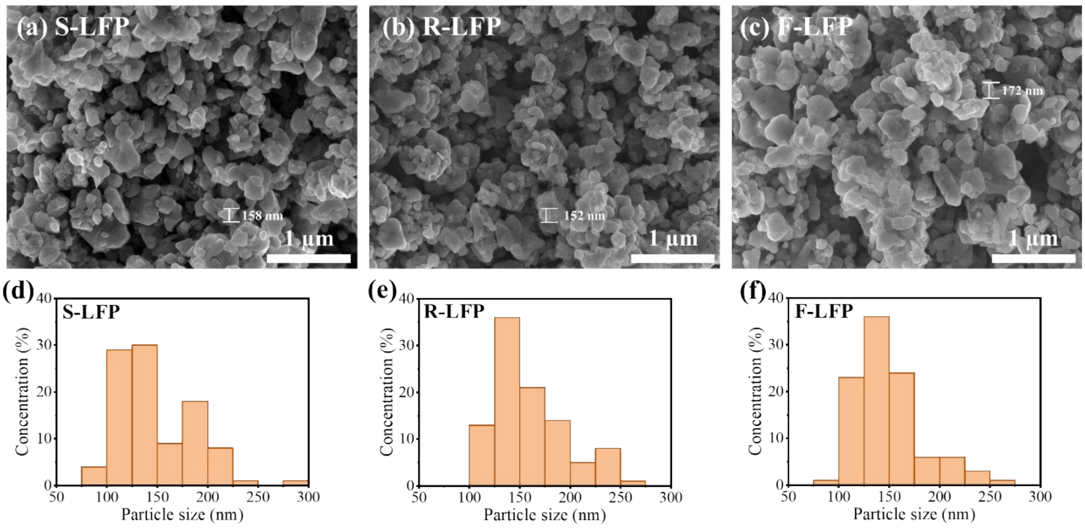

Fig. S5 SEM images and particle size distributions of different LFP samples. (a) and (d) S-LFP, (b) and (e) R-LFP, (c) and (f) F-LFP.

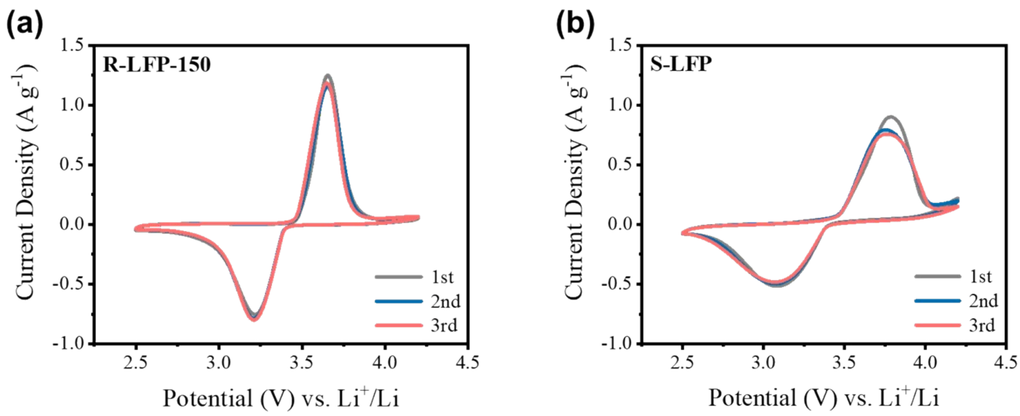

Fig. S6 CV curves of the first three cycles. (a) R-LFP-150, and (b) S-LFP with a scan rate of 0.5 mV s^{-1} in the potential range of 2.5-4.2 V (vs. Li^+/Li).

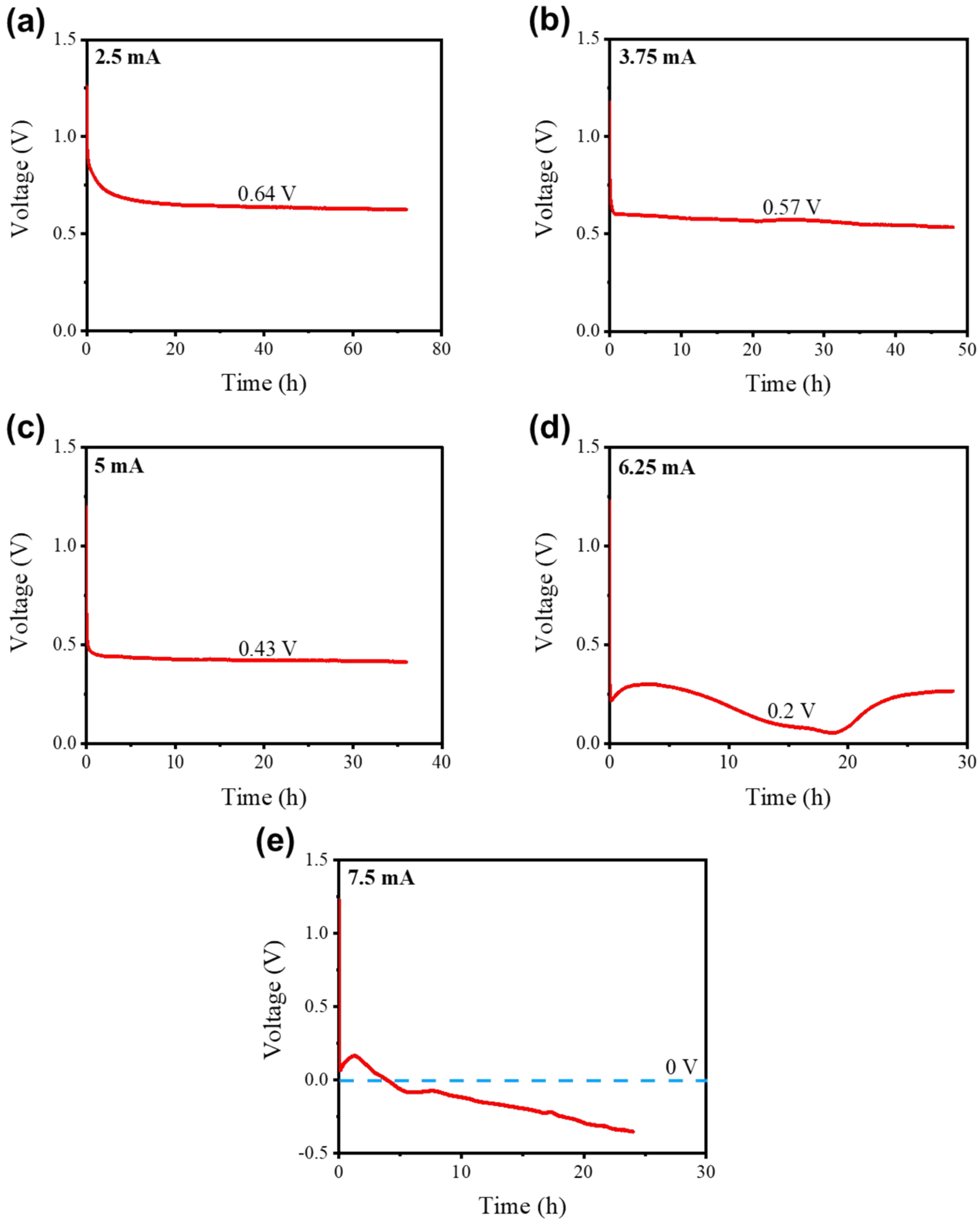

Fig. S7 The Discharge curves of re-lithiation process at different current. (a) 2.5 mA, (b) 3.75 mA, (c) 5 mA, (d) 6.25 mA, and (e) 7.5 mA.

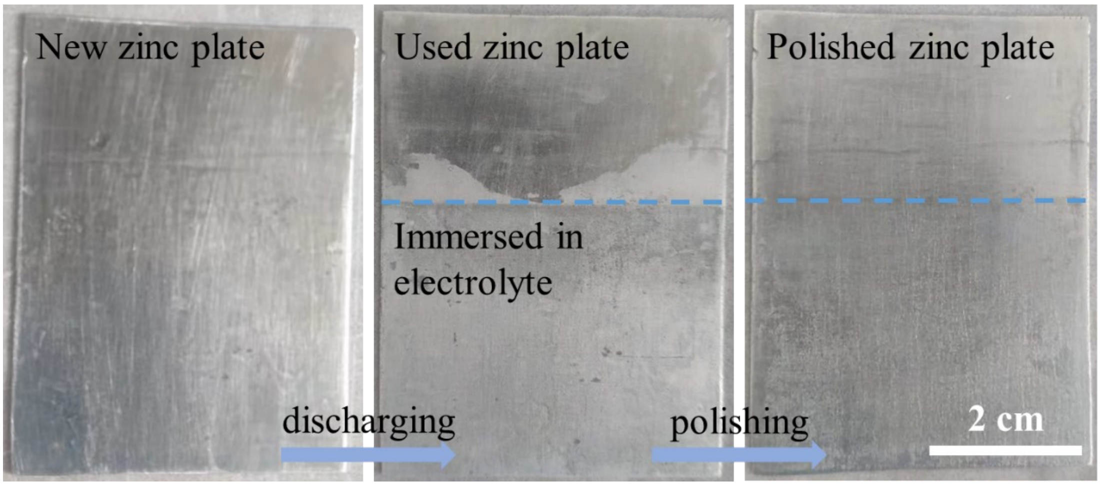

Fig. S8 Zinc plate anode at different states.

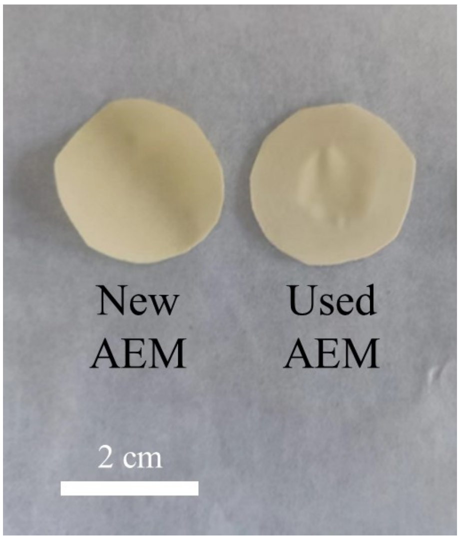

Fig. S9 The anion-exchange membrane (AEM) at different states.

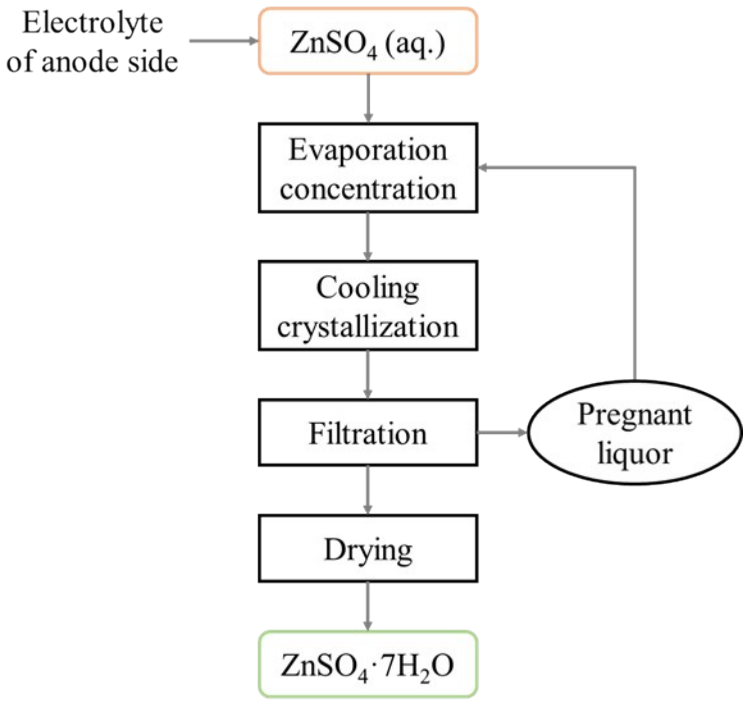

Fig. S10 The flow chart of recycling $ZnSO_4$ in anode electrolyte.

Table S1. Lithium element content in S-LFP and R-LFP recycled at different TIA.

LFP samples	S-LFP	80%	100%	150%	300%
Lithium content (wt.%)	3.38	3.64	3.67	3.81	3.68

Table S2. Lithium element content in S-LFP and R-LFP recycled at different current.

LFP samples	S-LFP	2.5 mA	3.75 mA	5 mA	6.25 mA
Lithium content (wt.%)	3.38	3.46	3.53	3.81	3.95

Table S3. The Warburg factor (σ) and lithium ion diffusion coefficient (D_{Li^+}) of S-LFP and R-LFP recycled at different TIA.

LFP samples	σ / Ω	D_{Li^+} / cm^2 s^{-1}
S-LFP	233	1.23×10^{-16}
80%	107	5.81×10^{-16}
100%	100	6.65×10^{-16}
150%	64	1.62×10^{-15}
300%	128	4.06×10^{-16}

Table S4. The Warburg factor (σ) and lithium ion diffusion coefficient (D_{Li^+}) of S-LFP and R-LFP recycled at different current.

LFP samples	σ / Ω	D_{Li^+} / cm$^{2\ -1}$
S-LFP	233	1.23×10^{-16}
2.5 mA	160	2.60×10^{-16}
3.75 mA	112	5.30×10^{-16}
5 mA	64	1.62×10^{-15}
6.25 mA	76	1.15×10^{-15}

Table S5. The initial coulombic efficiency (ICE) of S-LFP and R-LFP recycled at different TIA.

LFP samples	S-LFP	80%	100%	150%	300%
ICE	82.2%	97.7%	92.6%	94.6%	99.7%

Table S6. The ICE of S-LFP and R-LFP recycled at different current.

LFP samples	S-LFP	2.5 mA	3.75 mA	5 mA	6.25 mA
ICE	82.2%	92.7%	92.6%	94.6%	95.3%

Table S7. The cost to recycle 1 ton of S-LFP cathode material.

	Unit price	Dosage	Cost ($)
S-LFP	1406 $/t [1]	1 t	1406
$Li_2SO_4 \cdot H_2O$	2270 $/t [2]	0.1533 t	347.0
electric energy	0.08 $/kW·h [3]	20.25 kW·h	1.62
Total cost			**1755**

Table S8. The relevant data about the recent development in the direct recycling methods of LFP.

Raw materials	Treatment methods and conditions	Electrochemical performance of R-LFP	Ref.
Spent $LiFePO_4$ (S-LFP)	Heat-treatment at 650°C for 1 h, Ar/H_2	135.0 mAh g^{-1} at 1 C	4
S-LFP and Fresh LFP	Heat-treatment at 700°C for 8 h, N_2	144.0 mAh g^{-1} at 0.1 C, 97.0% after 100 cycles	5
S-LFP and Li_2CO_3	Heat-treatment at 650°C for 1 h, Ar/H_2	147.3 mAh g^{-1} at 0.2 C, 95.3% after 100 cycles	6
S-LFP and Li/Fe/P source	Heat-treatment at 650°C for 10 h, N_2	139.0 mAh g^{-1} at 0.2 C, 95.0% after 100 cycles	7
S-LFP, LiOH and graphene oxide	Hydrothermal at 160°C for 6h	150.4 mAh g^{-1} at 0.5 C, almost 100% after 300 cycles	8
S-LFP and Li_2SO_4	Hydrothermal at 200°C for 3h	141.9 mAh g^{-1} at 1 C, 98.6% after 200 cycles	9
S-LFP, LiOH and Li_2CO_3	Hydrothermal at 180°C for 5h and annealing with Li_2CO_3 at 600°C for 2h	159.0 mAh g^{-1} at 0.5 C and 144.0 mAh g^{-1} at 2 C, 93.7% after 300 cycles	10
S-LFP and $Li_2C_2O_4$	In situ electrochemical process by pre-lithiation separator	138.0 mAh g^{-1} at 1 C, 83.5% after 150 cycles	11
S-LFP and Li_2SO_4	Electrochemical relithiation by discharging the electrolytic tank	134.0 mAh g^{-1} at 1 C, 85.5% after 300 cycles	Our work

Table S9. The lithium content in the cathode and anode electrolyte after discharging.

Electrolyte at different state	lithium concentration (mol L^{-1})
Cathode electrolyte before discharging (1 mol L^{-1} Li_2SO_4)	2
Anode electrolyte before discharging (0.1 mol L^{-1} $ZnSO_4$)	0
Cathode electrolyte after discharging	1.880
Anode electrolyte after discharging	0.03588

Calculation of current efficiency based on the change of the Li^+ concentration:

The Li^+ concentration of cathode and anode electrolyte respectively after discharging at the best condition are presented in the **Table S9**. Obviously, the lithium concentration decreases to 1.880 mol L^{-1} after discharging, the loss of lithium can be divided into two parts, one is intercalated into S-LFP to achieve relithiation, the other migrates to the anode electrolyte, which cannot be recycled due to far low concentration (0.03588 mol L^{-1}), but this part will affect the utilization efficiency of lithium. In addition, the theoretical consumption of lithium element when recycling 1 mol S-LFP is 0.264 mol, so the theoretical consumption of lithium element when recycling 4 g S-LFP in this experiment is 0.0067 mol. Therefore, the current efficiency (η) based on the change of the Li^+ concentration can be calculated as follows:

$$\eta = \frac{0.0067}{(2-1.88)*80*10^{-3}}*100\% = 70\%$$

where 0.0067 mol is the theoretical consumption of lithium, (2 mol L^{-1}-1.88 mol L^{-1}) *80 mL*10^{-3} is the practical consumption of lithium in the recycling process.

Calculation of costs:

(1) **The cost of raw materials.** The cost of S-LFP cathode material pre-treated in the industry is 1406 $/t.

(2) **The cost of reagent.** According to the unit price and dosage of the reagent listed in **Table S7**, the cost of reagent for the optimal recycling parameters (150%-TIA and 5 mA of discharge current) is calculated as follows:

1-theoretical consumption of lithium element when recycling 1 mol S-LFP:

30 mAh g^{-1} * 150% / 170 mAh g^{-1} = 0.2647 mol

2-practical consumption of lithium element when recycling 1 mol S-LFP:

0.2647 mol / 70% = 0.3781 mol

3- practical consumption of $Li_2SO_4·H_2O$ when recycling 1-ton S-LFP:

(0.3781 mol * 127.96 g mol^{-1}) / (2 * 157.76 g mol^{-1}) = 0.1533 t

4-cost of $Li_2SO_4·H_2O$ when recycling 1-ton S-LFP:

0.1533 t * 2270 \$/t = 347.0 \$

(3) **The cost of electric energy.** According to **Table S7**, the cost of electric energy for the optimal recycling parameters (150%-TIA and 5 mA of discharge current) is calculated as follows:

1-consumption of electric energy when recycling 4 g S-LFP with stable voltage of 0.45 V:

30 mAh g^{-1} * 150% * 4 g * 0.45 V = 8.100*10^{-5} kW·h

2-cost of electric energy when recycling 1-ton S-LFP:

8.1*10^{-5} kW·h * 1,000,000 g / 4 g * 0.08 \$/kW·h = 1.620 \$

It can be seen that the electric energy consumption is so low as to can be negligible.

The total cost of recycling 1-ton S-LFP cathode material:

1406 \$ + 347.0 \$ + 1.620 \$ ≈ 1755 \$

Calculation of benefits and profits:

When S-LFP is recycled by the proposed electrochemical re-lithiation method, almost all the S-LFP can be recovered due to the continuous magnetic stirring process at cathode of H-type electrolytic tank, so the recovery efficiency can be regarded as 100%, which means that 1-ton R-LFP with best electrochemical performance can be obtained when recycling 1-ton S-LFP. Because the average price of LFP used for energy storage is 7283.29 \$/t,[12] so the corresponding benefits and profits are calculated as follows:

(1) **Benefits.**

7283.29 \$/t * 1 t ≈ 7283 \$

(2) **Profits:**

7283 \$ - 1755 \$ = 5528 \$

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