Supporting Information

A paired electrolysis approach for recycling spent lithium iron phosphate batteries in an undivided molten salt cell

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Roasting experiment: A tube furnace was used for performing the molten salt roasting flowed with Ar. First, the $LiFePO_4$ powder was mixed with pre-mixed Na_2CO_3-K_2CO_3 salt at a certain mole ratio (n_{LiFePO_4}: $n_{CO_3^{2-}}$ = 1: 2), and then the mixture was ground together in a planetary ball mill for 4 h to ensure uniform mixing. Second, the well-mixed mixture was placed in tube furnace to conduct roasting. The temperature was raised to 750 °C at a heated rate of 5 °C min^{-1} under the protection of Ar and then roasting for 2 h at 750 °C. Finally, after the tube furnace cooled down, the product was taken out and then washed with deionized water to remove the soluble salt. The product drying at 80 °C for 12 h was then characterized.

The mixture of $LiFePO_4$ powder and graphite powder was also roasted for 2 h at 750 °C under Ar atmosphere, and the mass ratio of graphite/$LiFePO_4$ was 2: 1. Besides, the $LiFePO_4$ powder was roasted for 2 h at 750 °C in air and in Ar, respectively.

Supplementary figures

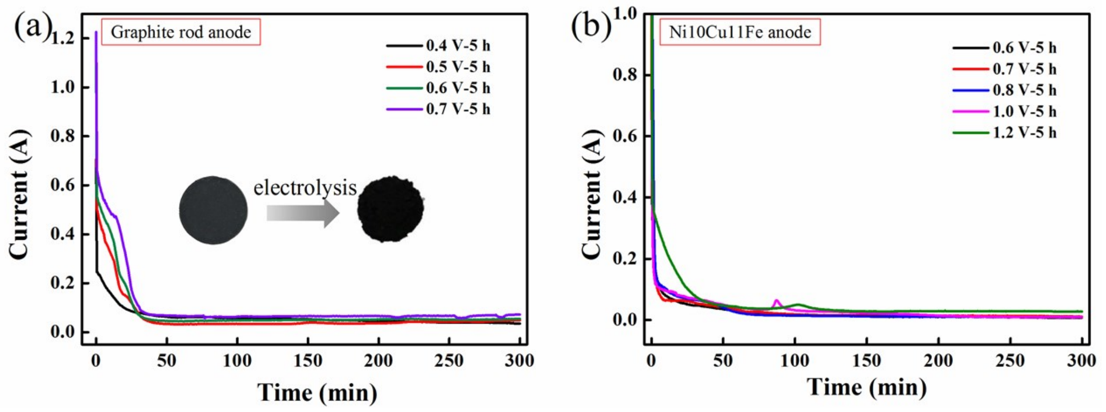

Fig. S1 Current profiles of the electrolyzer with a graphite anode (a) and Ni10Cu11Fe anode (b) under different cell voltages.

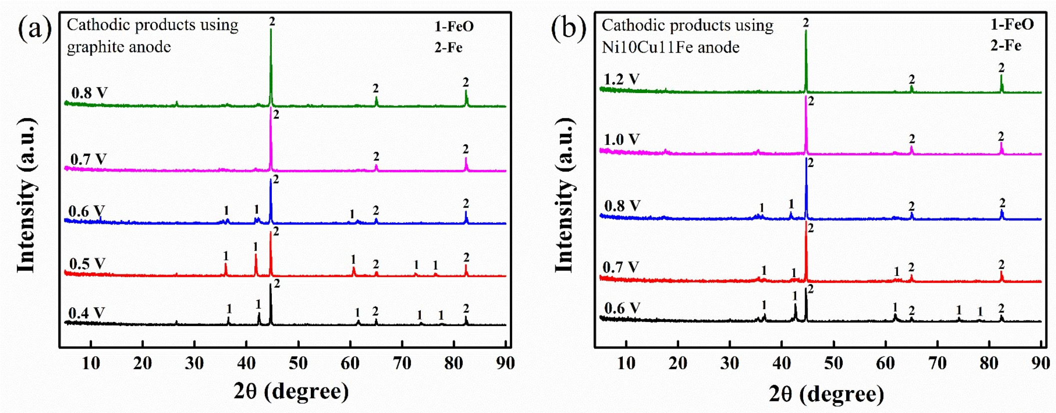

Fig. S2 XRD patterns of electrolytic products obtained under different cell voltages adopting graphite as the anode (a) and Ni10Cu11Fe alloy as the anode (b).

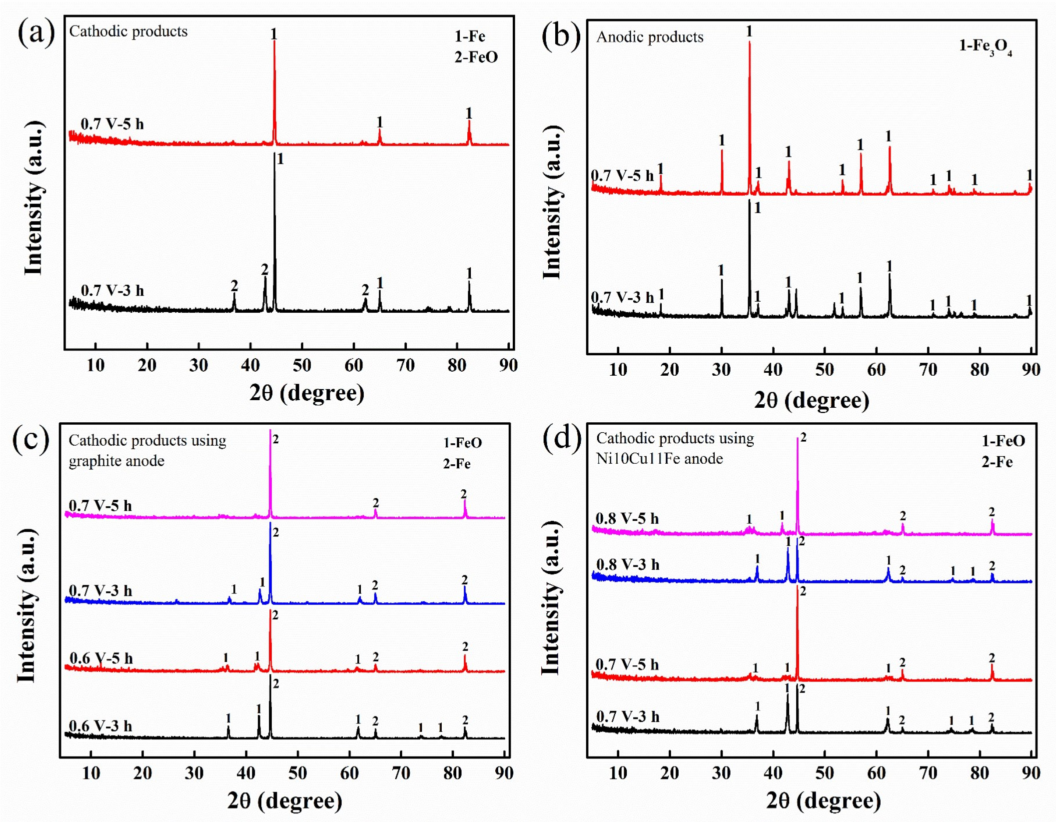

Fig. S3 XRD patterns of electrolytic cathodic/anodic products obtained at three different types of molten salt electrolyzers with a $LiFePO_4$ cathode coupling with the same $LiFePO_4$ anode (a, b), a graphite anode (c), and a Ni10Cu11Fe anode (d).

Energy efficiency calculation

Under the cell voltage of 0.7 V, the weight of dual $LiFePO_4$ electrodes was 2.91 g, and the electrodes was completely reduced to solid Fe and oxidized to solid Fe_3O_4, respectively. And 1 mol of $LiFePO_4$ consumes 0.5 mol of electrons. The energy consumption (E) is calculated by **equations** S**1** and S**2**:

$$E = U \times Q \tag{S1}$$

$$Q = n_e \times F \tag{S2}$$

where U is the applied cell voltage, Q is the consumed charge, n_e is the mole of transferring electrons and F is the Faraday constant.

$$Q = n_e \times F = \frac{1}{2} \times \frac{m_{LiFePO_4}}{M_{LiFePO_4}} \times F = \frac{1}{2} \times \frac{2.192}{157.76} \times 96485\ A \cdot s = 889.87\ A \cdot s$$

$$E = U \times Q = 0.7\ \times 889.87\ W \cdot s = 623.34\ W \cdot s\ =\ 0.173\ W \cdot h$$

According to the battery testing system, the recorded energy consumption (E_r) was 0.1929 W h. The energy efficiency (η) is calculated to 89.68% by **equation S3**.

$$\eta = \frac{E}{E_r} = \frac{0.173}{0.1929} = 89.68\%$$

(S3)

Economic evaluation

Assuming dealing with 1 kg of $LiFePO_4$ powder and the Li^+ recovery rate (r_{Li}) is 95.2%, the generated $NaLi_2PO_4$ mass ($m_{NaLi_2PO_4}$) can be calculated:

$$m_{NaLi_2PO_4} = \frac{m_{LiFePO_4}}{M_{LiFePO_4}} \times \frac{1}{2} \times M_{NaLi_2PO_4} \times 95.2\% = \frac{1000}{157.76} \times \frac{1}{2} \times 131.8 \times 95.2\% = 397.67\ g$$

And the precipitated Li_3PO_4 mass ($m_{Li_3PO_4}$) also can be calculated：

$$m_{Li_3PO_4} = \frac{m_{NaLi_2PO_4}}{M_{NaLi_2PO_4}} \times \frac{2}{3} \times M_{Li_3PO_4} = \frac{397.67}{131.8} \times \frac{2}{3} \times 115.7 = 232.73\ g$$

At the same time, the mass of generated Fe (m_{Fe}) and Fe_3O_4 ($m_{Fe_3O_4}$) can be calculated as 88.74 g and 367.65 g, respectively.

On the assumption, the total mass of Na_2CO_3-K_2CO_3 molten salt is 7 kg, and according to the molar ration (Na: K = 59: 41), the Na_2CO_3 and K_2CO_3 was weighed as 3672.46 g and 3327.54 g, respectively. The electrolysis was conducted under 0.7 V and the energy efficiency (η) is 89.68%. Therefore, the power consumption is calculated:

$$E = \frac{U \times Q}{\eta} = 0.7 \times \frac{1000}{157.76} \times \frac{1}{2} \times 96485 \div 89.68\% = 238690.62\ W \cdot s = 0.066\ Kw \cdot h$$

The costs of Na_2CO_3, K_2CO_3, Li_3PO_4, Fe powder and Fe_3O_4 are 2.12 \$/500g, 3.81 \$/500g, 28.68 \$/100g, 6.50 \$/500g and 13.28 \$/500g, respectively. And the price of electricity is 0.071 \$/kW h. So, the total cost (C_{total}) and total profit (P_{total}) are calculated:

$$C_{total} = C_{Na_2CO_3} + C_{K_2CO_3} + C_{electricity} = 3672.46 \times \frac{2.12}{500} + 3327.54 \times \frac{3.81}{500} + 0.066 \times 0.071 = 40.93\ \$$$

$$P_{total} = P_{Li_3PO_4} + P_{Fe} + P_{Fe_3O_4} = 232.73 \times \frac{28.68}{100} + 88.74 \times \frac{6.5}{500} + 367.65 \times \frac{13.28}{500} = 77.67\ \$$$

Therefore, the total processing revenue (P) can be obtained by treating 1 kg spent $LiFePO_4$ powder with paired electrolysis process:

$$P = P_{total} - C_{total} = 77.67 - 40.93 = 36.74\ \$$$

In summary, when dealing with 1 kg of spent $LiFePO_4$ powders, the total profit of whole processes in this study is around 36.74 \$.

Supplementary tables

Table. S1 Summary of reported approaches for recycling spent $LiFePO_4$ batteries.

Recycling method	Chemical agents	Recovery rates	Products	Ref.
Hydrometallurgy	0.3 M H_2SO_4 (H_2O_2/Li molar ratio 2.07, H_2SO_4/Li molar ratio 0.57, 60 °C, and 120 min), Na_3PO_4 as precipitant	Li 95.56%	$FePO_4 \cdot 2H_2O$ and Li_3PO_4	1
	0.8 M CH_3COOH as leaching agent, 6 vol% H_2O_2 as oxidant (S/L ratio of 120 g L^{-1}, 50 °C, 30 min), Na_2CO_3 as precipitant	Li 95.05%	$FePO_4$ and Li_2CO_3	2
	0.5 M H_3PO_4 as leaching agent with $LiFePO_4$/H_3PO_4 molar ratio of 1:3.16, at room temperature and 1 h	-	$FePO_4 \cdot 2H_2O$ and LiH_2PO_4	3
	EDTA-2Na as activation additive (cathode powder/EDTA-2Na mass ratio of 3:1, activation time of 2 h), 0.6 M H_3PO_4 as leaching agent (S/L ratio of 50 g L^{-1}, and leaching time of 20 min)	Fe 97.67% Li 94.29%	$FePO_4 \cdot 2H_2O$ and Li_3PO_4	4
	2.5 M H_2SO_4 (L/S ratio of 10 mL g^{-1}, 60 °C, 4 h), $NH_3 \cdot H_2O$ and Na_3CO_3 as precipitant	Li 97% Fe 98%	$FePO_4$ and Li_2CO_3	5
	1.05 times theoretical amount of $Na_2S_2O_8$ as leaching agent and oxidation agent (S/L ratio 300 $g \cdot L^{-1}$, 25 °C, 20 min), Na_2CO_3 as precipitant	Li 99%	$FePO_4$ and Li_2CO_3	6
	4M HCl, 6 M $NH_3 \cdot H_2O$ and Na_3PO_4 as precipitant	-	$FePO_4$ and Li_3PO_4	7
	H_2SO_4 and H_2O_2 as leaching agents, NaOH as precipitant, with $LiFePO_4$/H_2SO_4/NaOH molar ratio of 1:8:15	Fe 97.6% Li 96.9%	$Fe(OH)_3$, $FePO_4 \cdot 2H_2O$, and Li_3PO_4	8
	6 M HCl as leaching agent, 6.25% $NH_3 \cdot H_2O$ as precipitant	-	$FePO_4 \cdot 2H_2O$	9
Direct regeneration	heat-treatment cathode powders at 650 °C for 1 h under an Ar/H_2 flow	-	$LiFePO_4$	10
	soaking cathode plates in DMAC solvent at 30 °C for 30 min	-	$LiFePO_4$	11
	heating cathode scraps at 400−600 °C for 30 min under N_2	-	$LiFePO_4$	12
Mechanochemistry	NaCl as cogrinding reagent at room temperature, Na_2CO_3 as precipitant	-	$NaFePO_4$ and Li_2CO_3	13
	oxalic acid as cogrinding reagent and water leaching	Fe 94% Li 99%	$FeC_2O_4 \cdot 2H_2O$ and Li_3PO_4	14
Electrochemical method	0.20 M $K_3[Fe(CN)_6]$ as selective and regenerative redox mediator at a constant current of 5 mA cm^{-2}	-	$FePO_4$ and LiOH	15

Table S2. The environmental impact comparison of different methods for spent $LiFePO_4$ batteries.

Method	Operating condition	Waste generation	Energy source	Environmental footprint
Hydrometallurgy	Mild	Wastewater and waste gas	Chemical agents	Severe
Regeneration	High temperature	Less waste	Heat	Medium
Mechanochemistry	Mild	Less waste	Chemicals and ball-milling	Medium
Molten-salt paired electrolysis	Medium-high temperature	Partial waste gas	Electrons	Medium

References

1. H. Li, S. Xing, Y. Liu, F. Li, H. Guo and G. Kuang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 8017-8024.
2. Y. Yang, X. Meng, H. Cao, L. Xiao and Z. H. I. Sun, *Green Chem.*, 2018, **20**, 3121-3133.
3. D. Bian, Y. Sun, L. Sheng, T. Yuan, Z. Yang, X. Fan and W. Zhang, *Electrochim. Acta*, 2016, **190**, 134-140.
4. Y. Yang, X. Zheng, H. Cao, C. Zhao, X. Lin, P. Ning, Y. Zhang, W. Jin and Z. Sun, *ACS Sustainable Chem. Eng.*, 2017, **5**, 9972-9980.
5. R. Zheng, L. Zhao, W. Wang, Y. Liu, Q. Ma, D. Mu, R. Li and C. Dai, *RSC Adv.*, 2016, **6**, 43613-43625.
6. J. Zhang, J. Hu, Y. Liu, Q. Jing, C. Yang, Y. Chen and C. Wang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 5626-5631.

7. X. Wang, X. Wang, R. Zhang, Y. Wang and H. Shu, *Waste Manage.*, 2018, **78**, 208-216.

8. G. Cai, K. Y. Fung, K. M. Ng and C. Wibowo, *Ind. Eng. Chem. Res.*, 2014, **53**, 18245-18259.

9. E. J. Shin, S. Kim, J.-K. Noh, D. Byun, K. Y. Chung, H.-S. Kim and B.-W. Cho, *J. Mater. Chem. A*, 2015, **3**, 11493-11502.

10. J. Chen, Q. Li, J. Song, D. Song, L. Zhang and X. Shi, *Green Chem.*, 2016, **18**, 2500-2506.

11. X. Song, T. Hu, C. Liang, H. L. Long, L. Zhou, W. Song, L. You, Z. S. Wu and J. W. Liu, *RSC Adv.*, **7**, 4783-4790.

12. H. S. Kim and E. J. Shin, *Bull. Korean Chem. Soc.*, 2013, **34**, 851-855.

13. K. Liu, Q. Tan, L. Liu and J. Li, *Environ. Sci. Technol.*, 2019, **53**, 9781-9788.

14. E. Fan, L. Li, X. Zhang, Y. Bian, Q. Xue, J. Wu, F. Wu and R. Chen, *ACS Sustainable Chem. Eng.*, 2018, **6**, 11029-11035.

15. J. Yu, X. Wang, M. Zhou and Q. Wang, *Energy Environ. Sci.*, 2019, **12**, 2672-2677.