

Supporting Information

Towards economically feasible recycling of spent LiFePO₄ black mass: a thermodynamic-assisted targeted delithiation strategy

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Table. S1. Elemental content of spent LFP materials.

Elements	Li	Fe	P	Al	Mn	Cu
Content/wt%	4.26	35.8	19.08	0.53	0.04	0.51

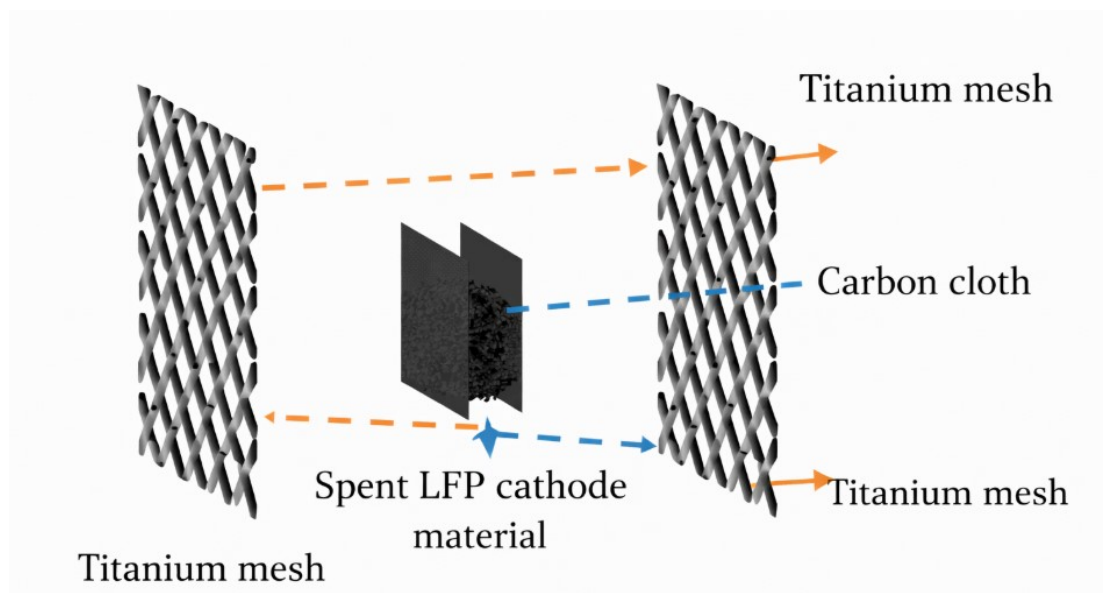


Fig. S1 Schematic illustration of anode electrode assembly

The thermodynamic data used in this work were obtained from published literature and the HSC Chemistry 10.0 database. Based on these data, the possible chemical reactions in the leaching system were identified, and the corresponding Gibbs free energy change (ΔG) and equilibrium constant (K) were calculated. The thermodynamic parameters at different temperatures were then determined according to Eqs. (12), (13), and (14). The detailed calculation procedure is described as follows.

Table S2 Chemicals, formulas, and reactions used in the thermodynamic calculations

Chemical Reactions	
$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	(1)
$Fe(OH)_2 + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$	(2)
$Fe^{3+} + e^- = Fe^{2+}$	(3)
$H_2O \leftrightarrow H^+ + OH^-$	(4)
$Fe(OH)_3 + 3H^+ + H_2PO_4^- \leftrightarrow FeH_2PO_4^{2+} + 3H_2O$	(5)
$Fe(OH)_3 + 3H^+ + 2H_2PO_4^- \leftrightarrow Fe(H_2PO_4)_2^+ + 3H_2O$	(6)
$Fe(OH)_3 + 3H^+ + HPO_4^{2-} \leftrightarrow FeHPO_4^+ + 3H_2O$	(7)
$Fe(OH)_3 + 3H^+ + 3H_2PO_4^- \leftrightarrow Fe(H_2PO_4)_3 + 3H_2O$	(8)
$Fe(OH)_2 + 2H^+ + H_2PO_4^- \leftrightarrow FeH_2PO_4^+ + 2H_2O$	(9)
$Fe(OH)_2 + 2H^+ + 2H_2PO_4^- \leftrightarrow Fe(H_2PO_4)_2 + 2H_2O$	(10)
$Fe(OH)_3 + 3H^+ + H_3PO_4 \leftrightarrow Fe(H_2PO_4)_2 + 3H_2O$	(11)
$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$	(12)
$\Delta G^\theta = -RT \ln K$	(13)
$\Delta G = \Delta G^\theta + RT \ln Q$	(14)

where ΔG is the Gibbs free energy change, Q is the reaction quotient, R is the molar gas constant

(8.31447 J/K·mol), T is the absolute temperature (K), ΔG_{θ} is the standard Gibbs free energy change (kJ·mol⁻¹), ΔH_{θ} is the standard enthalpy change (kJ·mol⁻¹), ΔS_{θ} is the standard entropy change (J·mol⁻¹·K⁻¹), and K is the equilibrium constant.

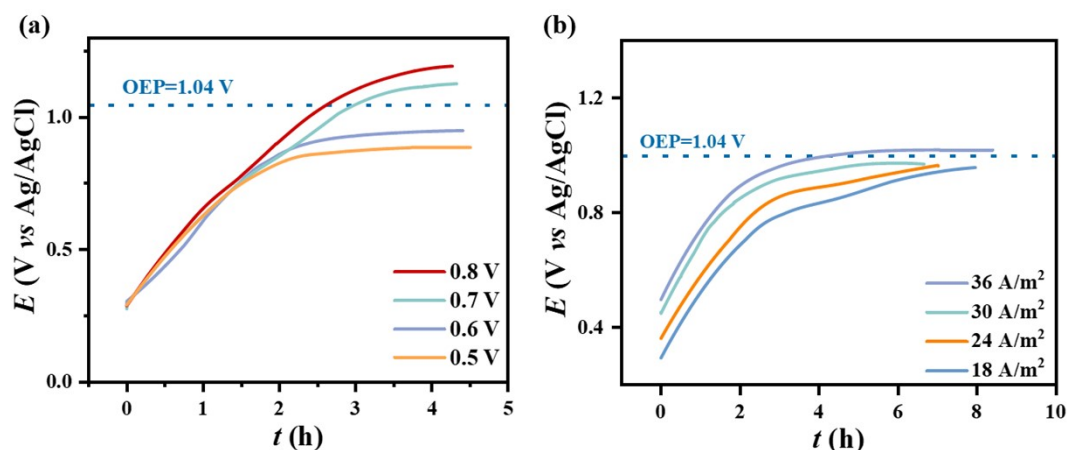


Fig. S2 Curves of anode potential at different cell voltages (a) and current density (b) with time.

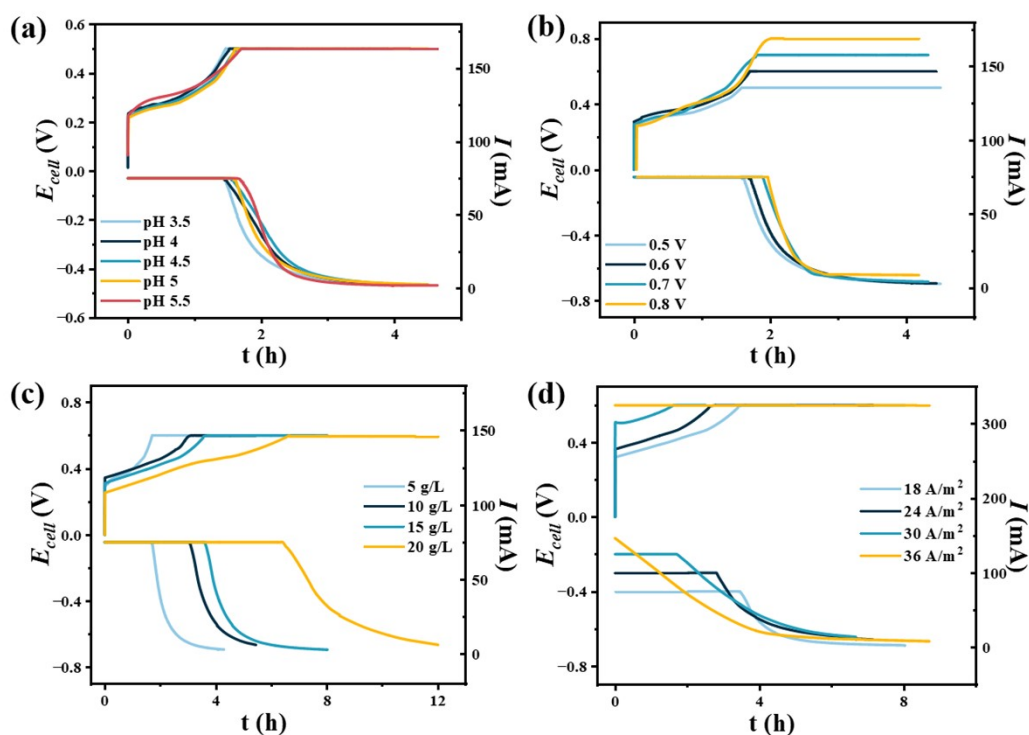


Fig. S3 Time-dependent variations of cell voltage and current under different operational conditions: (a) effect of solution pH; (b) influence of cell voltage; (c) impact of current density; (d) effect of solid-to-liquid ratio

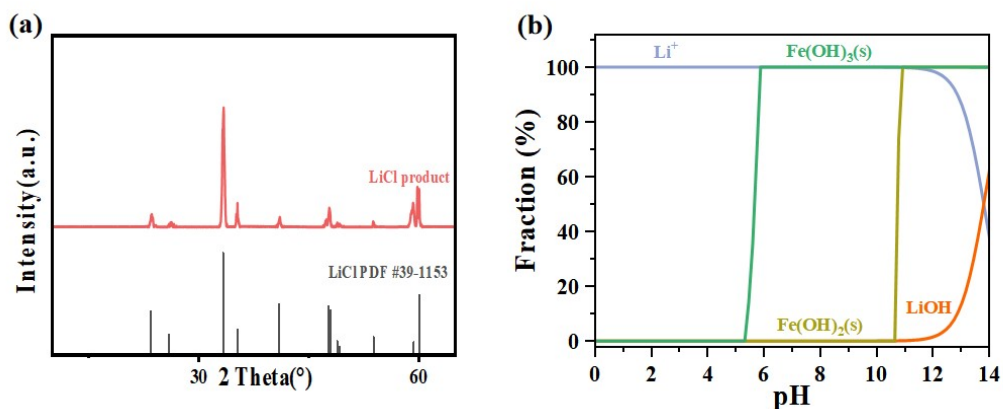


Fig. S4 Comparison of XRD images for lithium chloride product and reference card (a), Species distributions of Li^+ with varying pH and $\text{Fe}^{2+}/\text{Fe}^{3+}$ precipitation pH range (b).

Table S3 presents a preliminary economic comparison between the method developed in this study and the reported method in terms of product revenue, energy cost, and material consumption. It should be noted that the major reaction media and electrolytes in both electrochemical routes are potentially recyclable within the process, which is different from conventional acid-leaching systems where reagent consumption is usually explicit and continuous. Therefore, reagent cost was not separately discussed in this table. Instead, the analysis was performed based on parameters that are clearly available and reasonably comparable from the literature, including product revenue, energy cost, and electrode material consumption. Items lacking consistent reporting or those that could not be compared under similar system boundaries were not included, in order to maintain the clarity and rationality of the comparison. The prices of various products were checked from Internet. Besides, the calculation method of energy cost was referred from literatures^[1].

Table S3 Economic analysis for recycling 1 ton of scrap LiFePO₄ materials by the proposed process in China (exchange rate: 1 \$ = 6.90 CNY)

	This paper			Reported paper		
Revenue	Products	Mass (g)	Benefits (\$)	Products	Mass (kg)	Benefits (\$)
	LiCl	203.74	2384.88	Li ₂ CO ₃	169.81	2037.72
	FePO ₄	788.98	946.78	FePO ₄	728.29	873.948
				NaOH	200	80
Energy cost	Procedure	Consumption (kWh)	Cost (\$)	Procedure	Consumption (kWh)	Cost (\$)
	electrolysis	285.86	-12.879	Slurry electrolysis	1304.35	-195.65
	Evaporative crystallization	1100	-165	Evaporative crystallization	1100	-165
	Filtering and drying	230	-34.5	Filtering and drying	230	-34.5
Material consumption	Procedure	Area (m ²)		Procedure	Area(m ²)	
	Carbon fiber fabric	0.5	-433.56	Ru-Ti	0.25	-1070.26
Total profit			2685.721			1526.258

Reference

- (1) <https://chinese.alibaba.com/product-detail/Battery-Grade-Ferric-Phosphate-Raw-Material-1601125244817.html?spm=a27aq.29918103.4207392620.1.5c8750dfB65NF8&trafficsource=detail>
 - (2) https://www.alibaba.com/product-detail/Fast-Delivery-Best-Price-LiCl-Anhydrous_1600552057052.html?spm=a2700.galleryofferlist.normal_offer.d_image.413613a0ZmBedV&priceId=b496b9e0c6a944bc85a5fd792f1375ba
 - (3) https://www.alibaba.com/product-detail/KIG-Hot-Sales-Ruthenium-Plating-Titanium_1601224333587.html?spm=a2700.galleryofferlist.normal_offer.d_image.6e6b13a0rsgD9&priceId=b4e3bbe74834432382cf90fc4a432ac5
 - (4) https://www.alibaba.com/product-detail/KIG-Hot-Sales-Ruthenium-Plating-Titanium_1601224333587.html?spm=a2700.galleryofferlist.normal_offer.d_image.6e6b13a0rsgD9&priceId=b4e3bbe74834432382cf90fc4a432ac5
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