Electronic Supplementary Information (ESI)

Efficient Direct Regeneration of Spent $LiFePO_4$ from Various Degradation States for Sustainable Battery Recycling

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Experimental Section:

Chemical Reagents: oxalic acid (OA), dimethyl carbonate (DMC), and N-methl-2-pyrrolidone (NMP) were procured from Sigma-Aldrich. Lithium hydroxide monohydrate was procured from Alfa Aesar.

Spent LFP obtaining step: The 18650-type $LiFePO_4$ (LFP) cells were cycled to achieve a State of Health (SOH) between 55% and 70%. This cycling process simulates real-world usage conditions. The cells were discharged to 2 V before being opened with a tube cutter. Subsequently, the cathode, anode, and separator were manually separated. The cathodes were then fully soaked in dimethyl carbonate (DMC) under ultrasound for 16 minutes. This process was repeated twice to completely remove the residual salt from the cathode. After soaking, the wet cathodes were dried in a vacuum oven at 70°C for 2 hours. Once dried, the electrode coatings were manually peeled off from the current collector. The coating fragments were then mixed in N-methyl-2-pyrrolidone (NMP) and stirred at 70°C overnight to dissolve the PVDF. Finally, the S-LFP was collected after five rounds of washing with NMP and subsequent drying at 70 °C oven.

Regeneration Process: The regeneration process began with an ultrasound-assisted hydrothermal reaction. Initially, 0.20 M of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) and 0.1 M of oxalic acid (OA) were dissolved in deionized (DI) water using ultrasound. The spent $LiFePO_4$ (S-LFP) material (0.20 M) was then added to the prepared solution. The hydrothermal process was carried out with the power set to 300 W. The temperature was increased at a controlled rate of 15°C per minute to reach the desired reaction temperatures of 120°C, 150°C, and 180°C. The reaction was maintained for 1 hour at each of the specified temperatures. After the reaction, the temperature was allowed to return to room temperature naturally. The R-LFP was then collected by being washed three times with DI water followed by a final wash with ethanol. The washed R-LFP was then dried in an oven at 70°C.

Characterization: The S-LFP and R-LFP underwent a series of characterization using various techniques. Field emission scanning electron microscope (FESEM) analysis was carried out on a JEOL JSM 7600F SEM. Transmission electron microscope (TEM) analysis was performed on a FEI Titan monochromatic scnning TEM operating at 200 kV. X-ray diffraction (XRD) patterns were generated using a Bruker D8 Advance XRD equipped with Cu-Ka radiation of 1.5418 A, operated at 40 kV and 40 mA. X-Ray Photoelectron spectroscopy (XPS) measurements were carried out using a Kratos AXIS Supra+ X-Ray Photoelectron Spectrometer System (Kratos Analytical Ltd, UK) with a large 500 mm Rowland circle monochromated Al Ka (1486.6 eV) X-ray source. Energy-dispersive X-ray spectroscopy (EDX) was conducted using a JEOL 7600F Field Emission Scanning Electron Microscope fitted with an Oxford energy-dispersive X-ray detector.

Electrochemical performance Analysis: The R-LFP and S-LFP were combined with Denka Carbon and PVDF in a mass ratio of 90:5:5. The PVDF was pre-dissolved in NMP at a concentration of 5 wt%. After mixing the slurry using a Thinky mixer, the electrode slurry was coated onto aluminum foil using a doctor blade set to a thickness of 250 µm. The coated electrodes were then dried in an oven at 70°C overnight. Subsequently, the electrodes were cut into 12 mm round disks with a mass loading of approximately 3 mg/cm². These disk electrodes were transferred to an argon-filled glovebox for coin cell assembly. The half coin cells were assembled using lithium foil as the counter and reference electrodes, and the disk electrode as the working electrode. The cells were filled with 120 µL of 1.3 M $LiPF_6$ in EC/DEC (1:1 by volume) with an addition of 10 wt% FEC. Galvanostatic charge-discharge, rate, and cycling performance tests were conducted under ambient conditions at various current rates, within a voltage range of 2.7 to 4.2 V, using LANDHE battery testing equipment. Additionally, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed using an Autolab (Metrohm PGSTAT302N) workstation.

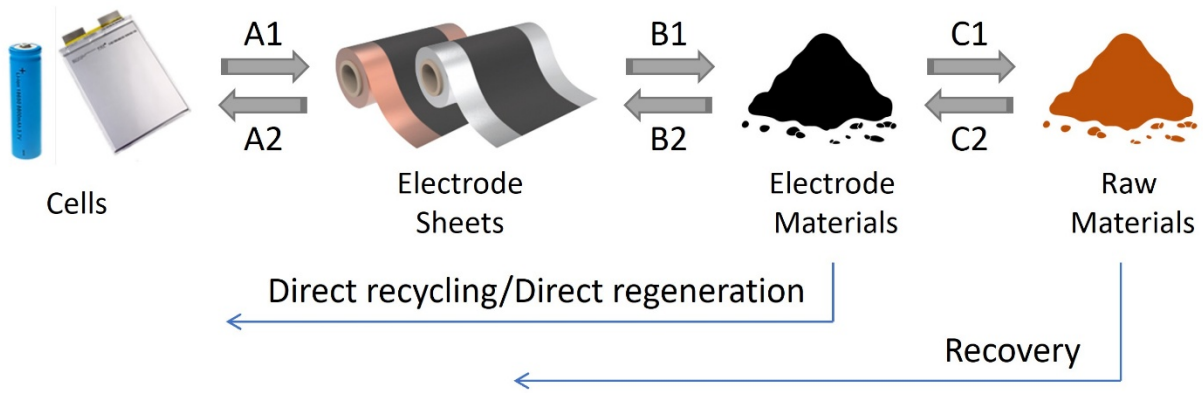


Figure S1: Illustration of the advantages of direct regeneration compared to recycling to raw materials. Beyond the value differences between electrode materials and raw materials, direct regeneration also saves manufacturing costs in the C2 step.

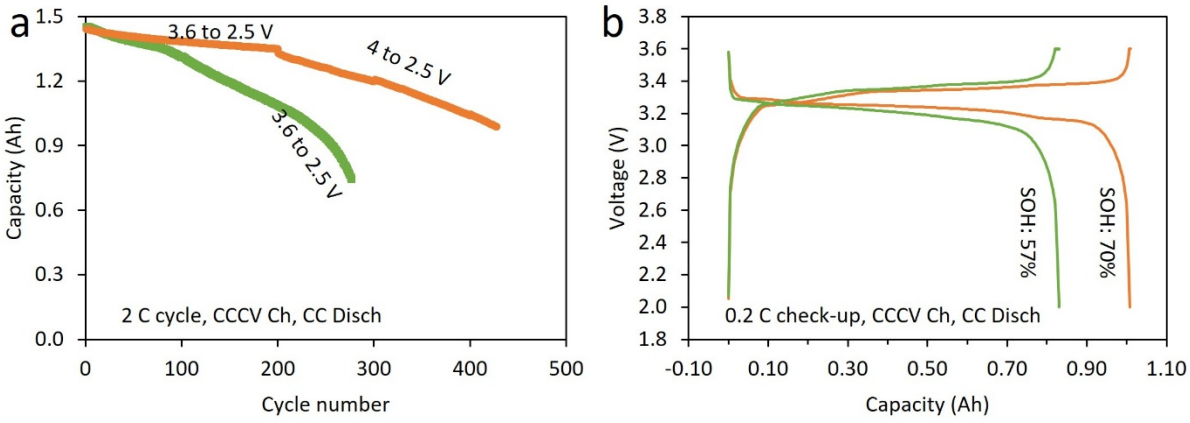


Figure S2. (a) Cycling of 18650-type $LiFePO_4$ cells (1.5 Ah). (b) Check-up of these cells after cycling test.

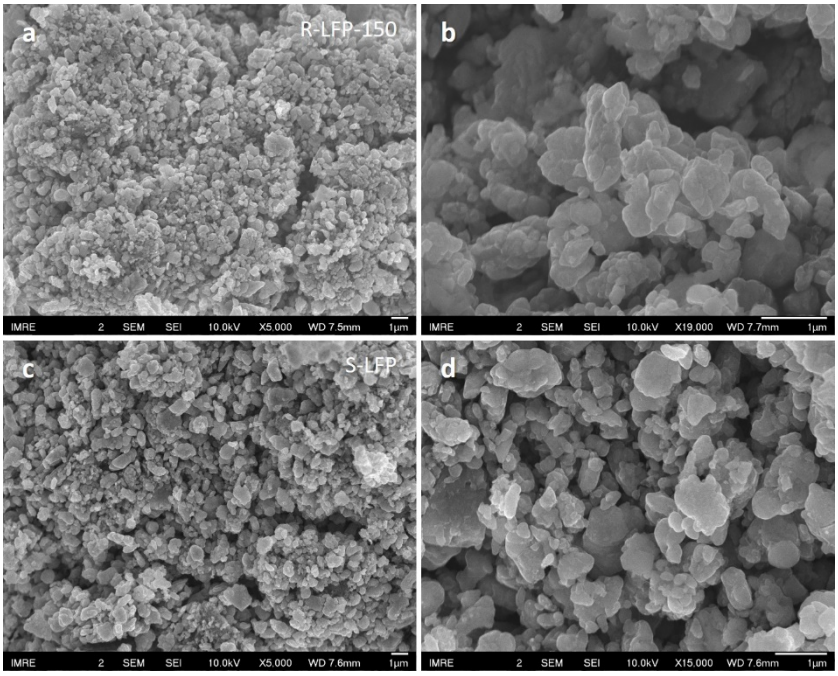
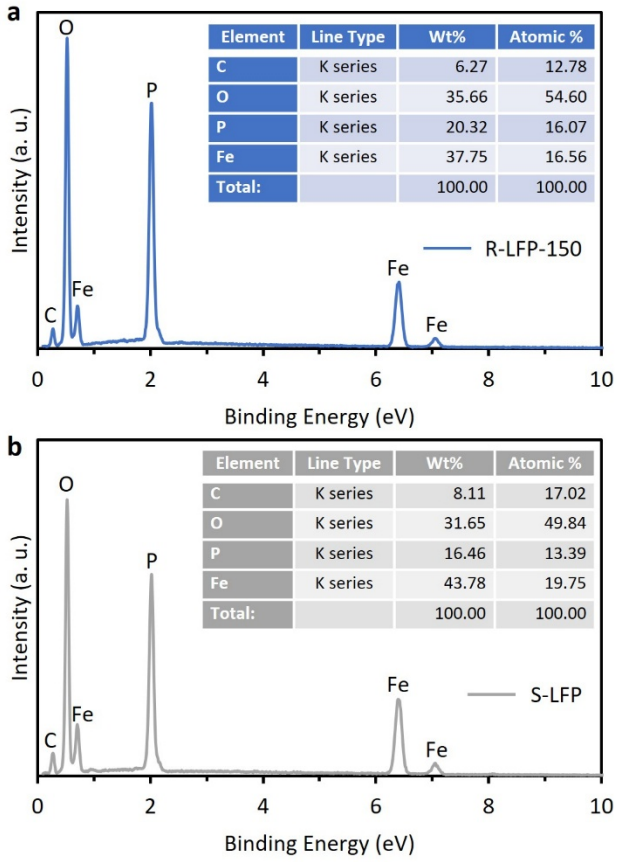


Figure S3: FESEM images of R-LFP-150 (a,b), S-LFP (c,d).



Element	Line Type	Wt%	Atomic %
C	K series	6.27	12.78
O	K series	35.66	54.60
P	K series	20.32	16.07
Fe	K series	37.75	16.56
Total:		100.00	100.00

Element	Line Type	Wt%	Atomic %
C	K series	8.11	17.02
O	K series	31.65	49.84
P	K series	16.46	13.39
Fe	K series	43.78	19.75
Total:		100.00	100.00

Figure S4. EDX spectra of R-LFP-150 and S-LFP.

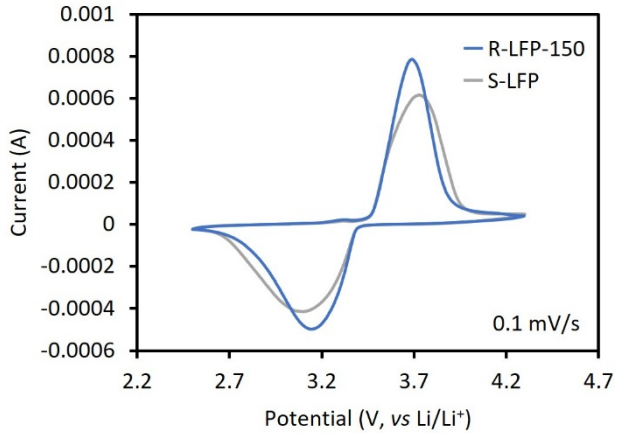


Figure S5: Cyclic voltammograms of R-LFP-150 and S-LFP.

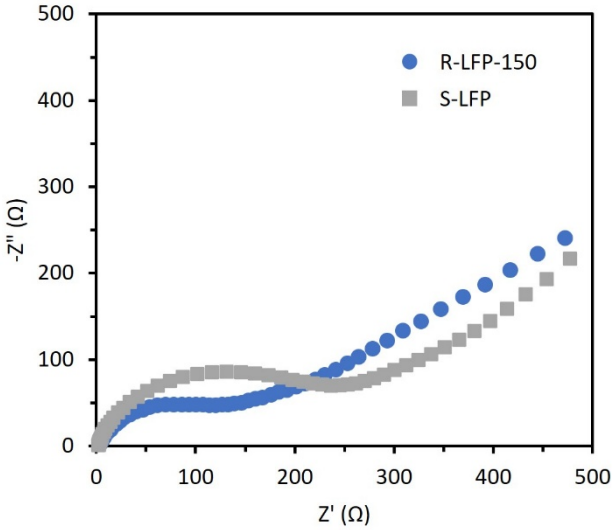


Figure S6: Impedance spectra of R-LFP-150 and S-LFP within a frequency range of 100 kHz to 10 mHz at open circuit voltage after 2 cycle CV test.

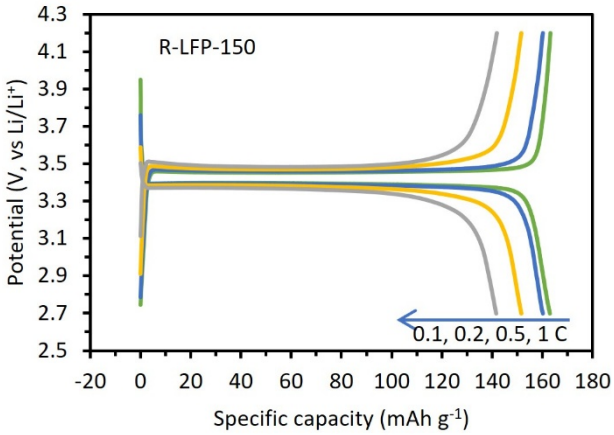


Figure S7: Charge/discharge profiles of R-LFP-150 at different current rates.

Table S1: Calculation of End-of-Product Price of Recycling 1 mt of spent LFP based on 4 May 2025

Product name	Molecular mass (g/mol)	mt	Price USD/mt	Product price of Recycling 1 mt of spent $LiFePO_4$
$LiFePO_4$	157.76	1	4504 [1]	4504
$LiOH \cdot H_2O$	41.96	0.266	8498 [2]	2260
Li_2CO_3	73.891	0.234	9080 [3]	2126

Table S2: Comparison of Microwave-Assisted Hydrothermal Treatment with Solid-Phase and Electrochemical Regeneration Methods.

Method	Energy Efficiency	Cost-Effectiveness	Environmental Impact	Key Notes
Microwave-Assisted Hydrothermal	High (rapid, localized heating, short reaction time)	High (lower operational cost due to shorter time and moderate conditions)	Low (reduced chemical use, low wastewater)	Fast kinetics, uniform heating, scalable
Solid-Phase Regeneration	Low (requires >600 °C, long heating)	Low (high energy consumption increases costs)	High (high CO_2 emissions, thermal degradation risks)	Simpler equipment but energy-intensive
Electrochemical Regeneration	Medium (depends on current efficiency)	Medium to Low (complex setup, high electricity cost)	Medium (possible chemical contamination, electrode consumption)	High purity achievable but costly and complex
Conventional Hydrothermal	Medium (requires longer heating, higher energy)	Medium (moderate pressure/temperature but long reaction time)	Low (reduced chemical use, low wastewater)	Widely studied, but slower and less efficient

Reference:

1. https://www.metal.com/Lithium%20Battery%20Cathode%20Precursor%20and%20Material/202006100013

2. https://www.metal.com/Lithium/201102250281
3. https://www.metal.com/Lithium/201102250059