Supporting Information

Manuscript ID:

Title: Rapid Room-Temperature Repair of Spent Lithium Iron Phosphate via Redox Mediators

Jinsuo Zhang,[#a] *Xinlong Chen,*[#a] *Ge Qu,* [a] *Shiqi Li,* [a] *Wang Wan,* [a] *Yunhui Huang,*[*b] *and Chao Wang*[*a]

a. School of Materials Science and Engineering, Tongji University, Shanghai 201804, China.

E-mail: chaow@tongji.edu.cn

b. School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China.

E-mail: huangyh@hust.edu.cn

# These authors contributed to this work equally.

The Supporting information includes:

Section S1. Experimental Section

Material Preparation

The lithium-deficient $LiFePO_4$ was prepared by immersing commercial $LiFePO_4$ powder (Shuangdeng Group) in a stoichiometric 1 M aqueous ammonium persulfate ($(NH_4)_2S_2O_8$) solution. The spent $LiFePO_4$ (S-LFP) material was obtained from disassembled LFP||Gr pouch cells (Wanxiang A123 Systems Corp). The specific procedure involved discharging the pouch cell to 1 V, followed by disassembly in an argon-filled glovebox. The spent electrode sheets were acquired by washing the separated electrode coatings with dimethyl carbonate (DMC), and the spent powder was obtained by pulverizing the detached coating material using a mechanical grinder. The spent powder was regenerated using 0.1 M LiI + 0.1 M C_2H_5OLi ethanol solution. The treatment time is set to 5 and 10 minutes, and the obtained regenerated powder is denoted as R-LFP-5min and R-LFP-10min, respectively. The direct regeneration of spent LFP electrodes is divided into two steps: the electrode immersion and iodide ion recovery. Firstly, the electrode is immersed in a 0.1M LiI + 0.1 M $LiNO_3$ ethanol solution. After removing the electrode, 0.1M C_2H_5OLi or 0.1M LiOH is introduced to recover iodide ions. Lithium iodide (LiI), lithium nitrate ($LiNO_3$), and lithium hydroxide (LiOH) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. Anhydrous ethanol and lithium ethoxide were sourced from Adamas.

Electrode Preparation and Cell Assembling

The LFP electrodes were prepared by mixing the LFP powder with Super P conductive carbon black (Shenzhen Kejing Co.) and polyvinylidene fluoride (PVDF 6020, binder, Solvay) in a weight ratio of 8:1:1 using N-methyl pyrrolidone (NMP) as the solvent. The resulting slurry was then cast on an Al foil with a thickness of 200 μm. After being subjected to a drying temperature of 80 °C for 12 hours, the electrodes underwent shaping into circular disks with a diameter of 12 mm to facilitate their assembly into coin cells. The same treatment is applied to the electrodes of direct regeneration. In an argon glovebox, 2025-type coin cells were fabricated. Each cell utilized 40 μL of electrolyte and a single piece of PP separator with a diameter of 16.5 mm. The electrolyte for the batteries was 1 M $LiPF_6$ in EC:DMC: EMC = 1:1:1 vol% with 2% VC. Then the spacer and the spring were added. The cell was sealed under a packaging pressure of 50 MPa.

Electrochemical Test

All batteries were allowed to rest for 2 hours before testing and then evaluated in a steady-temperature NEWARE Battery Test System (MIHW-200-160CH, 298 K, Shenzhen, China) with a voltage range of 2.8 to 3.9 V. Before cycling or rate performance tests, the batteries underwent formation at 0.1C for 3 cycles. During the 10C long-term cycling test, the batteries were charged via constant current (CC) to 3.9 V, followed by constant voltage (CV) charging at 3.9 V until the total charging duration reached 6 minutes. For the linear sweep voltammetry (LSV) measurements in solution, inert Pt electrodes served as the working and counter electrodes, with a saturated calomel electrode (SCE) as reference electrode and a scan rate of 1 mV/s. In the cyclic voltammetry (CV) tests of $LiFePO_4$ in aqueous and ethanol-based electrolytes, the working electrode was $LiFePO_4$, the counter electrode was lithium-deficient $LiFePO_4$, and the reference electrode was SCE. The electrolytes comprised either a 1 M $LiNO_3$ aqueous solution or a 1 M LiTFSI ethanol solution, with a scan rate of 0.1 mV/s in both cases. Electrochemical impedance spectroscopy (EIS) curves were all carried out on an electrochemical work station (GAMRY INTERFACE 1010E). The frequency range of EIS was from 0.1 Hz to 100,000 Hz.

Characterization Method

XRD measurements were carried out on a Bruker D8-Advance powder X-ray diffractometer operating at 40 kV and 40 mA, using Cu Kα radiation (λ= 0.15 405 nm). Confocal Laser Micro-Raman Spectrometer (Model: LabRAM HR Evolution) with a 532 nm excitation wavelength. Fourier-transform Infrared Spectrometer (Model: INVENIO). Inductively Coupled Plasma Optical Emission Spectrometer (Model: PE 7000).

Section S2. Supplementary Figures

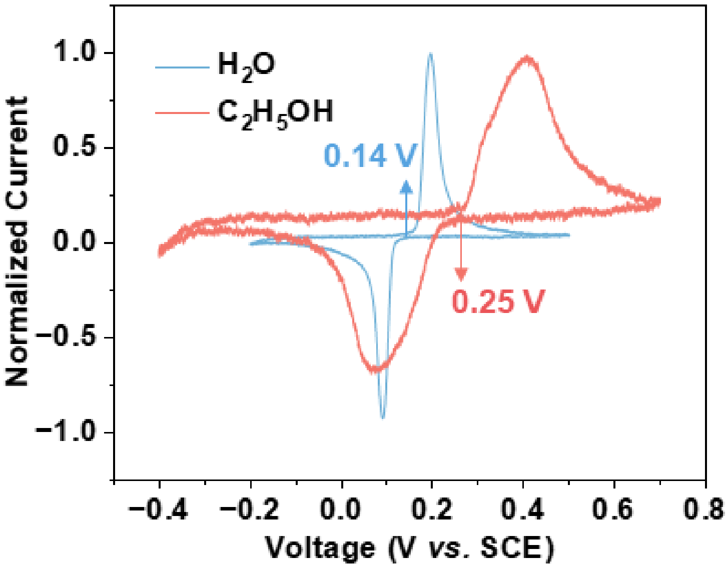

Fig. S1 The CV curves of LFP in 1M $LiNO_3$ in water and 1M LiTFSI in C_2H_5OH.

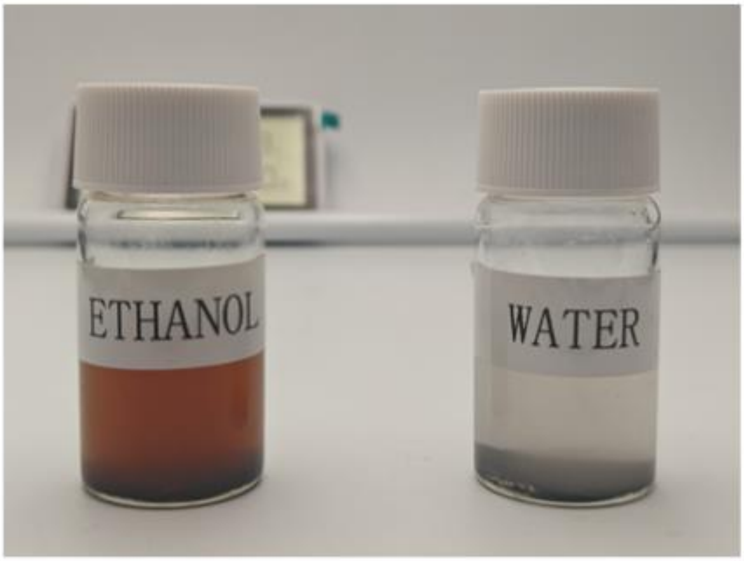

Fig. S2 The immersion of LFP-0.8 in 0.1M LiI ethanol solution and aqueous solution.

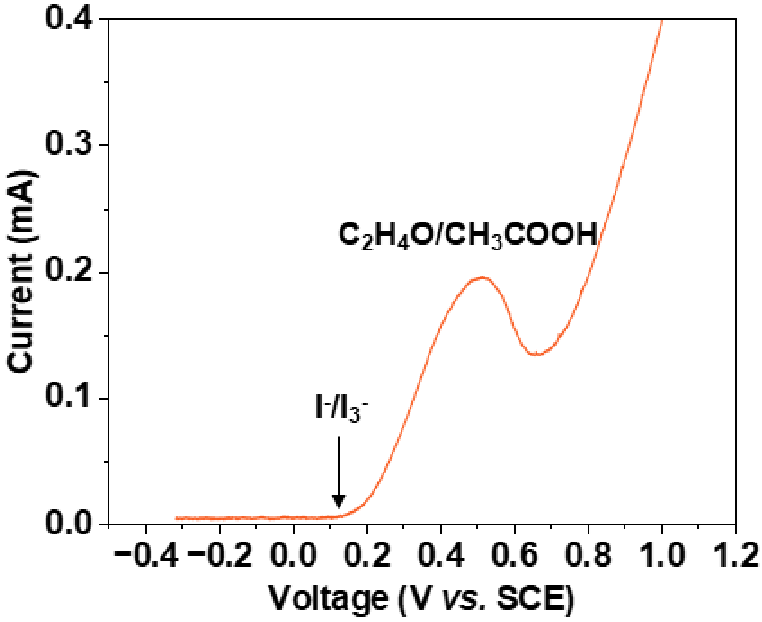

Fig. S3 The LSV profile of 1M LiI + 1M C_2H_5OLi ethanol solution.

Fig. S4 The immersion of LFP-0.8 in 0.1M LiI and 0.1M LiI + 0.1M C_2H_5OLi ethanol solutions, before (left) and after (right).

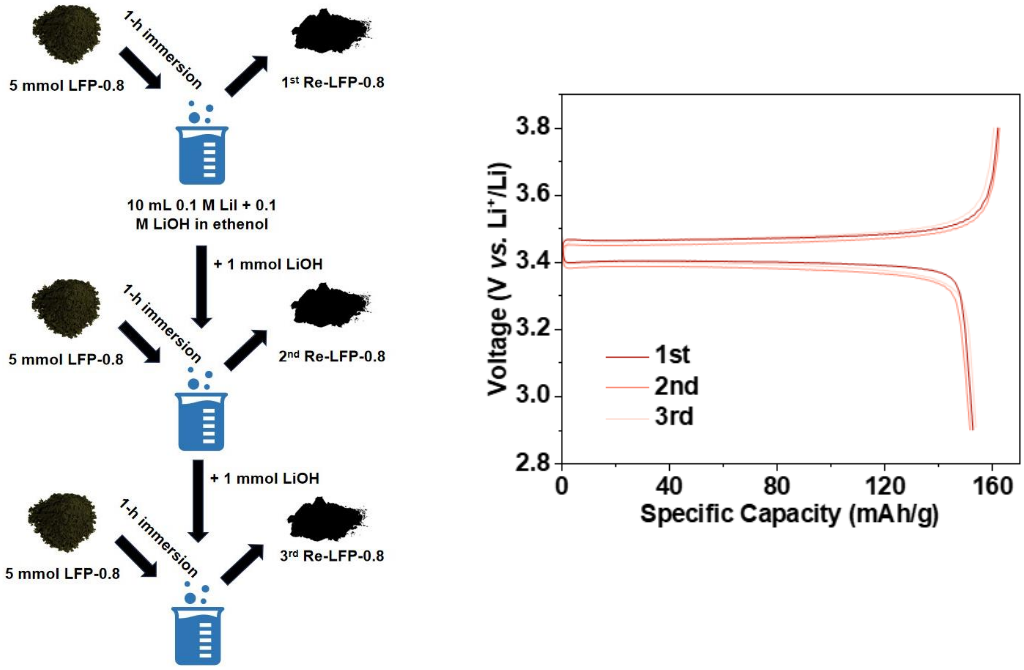

Fig. S5 The first-cycle charge and discharge curves of regenerated LFP-0.8 during three processes.

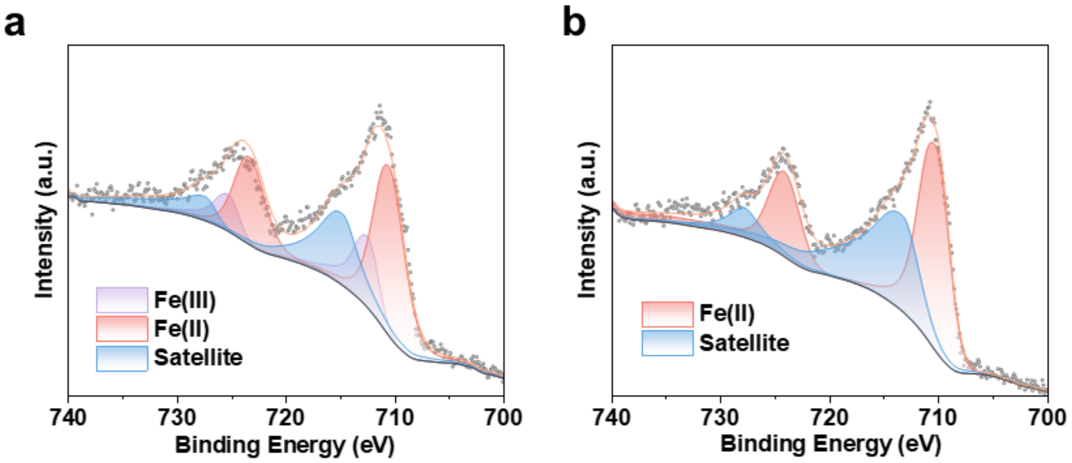

Fig. S6 The XPS results of S-LFP (a) and R-LFP-10min (b).

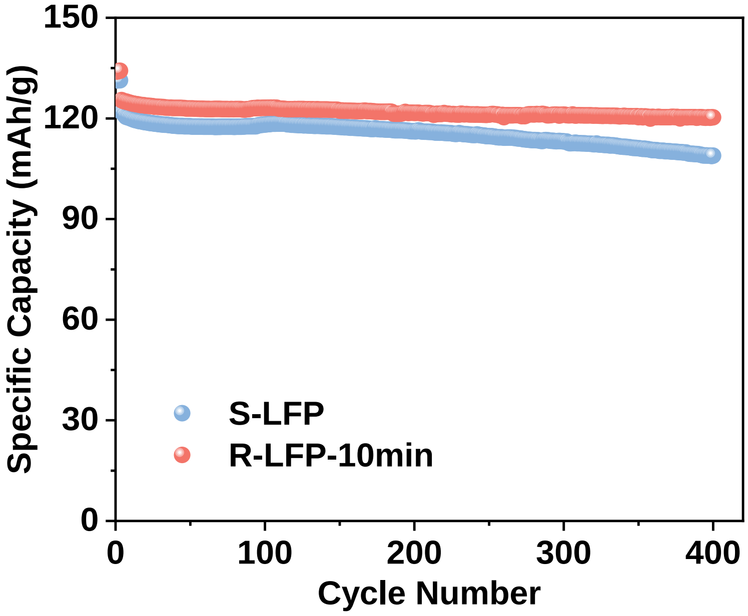

Figure S7. The cycle performance of S-LFP and R-LFP-10min under 1C for 400 cycles.

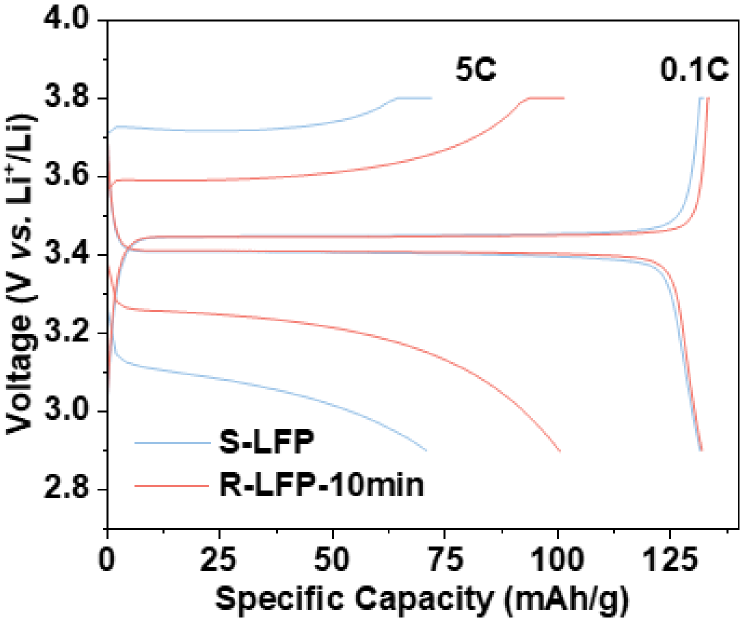

Fig. S8 The charge and discharge curves of S-LFP and R-LFP-10min at 0.1C and 5C.

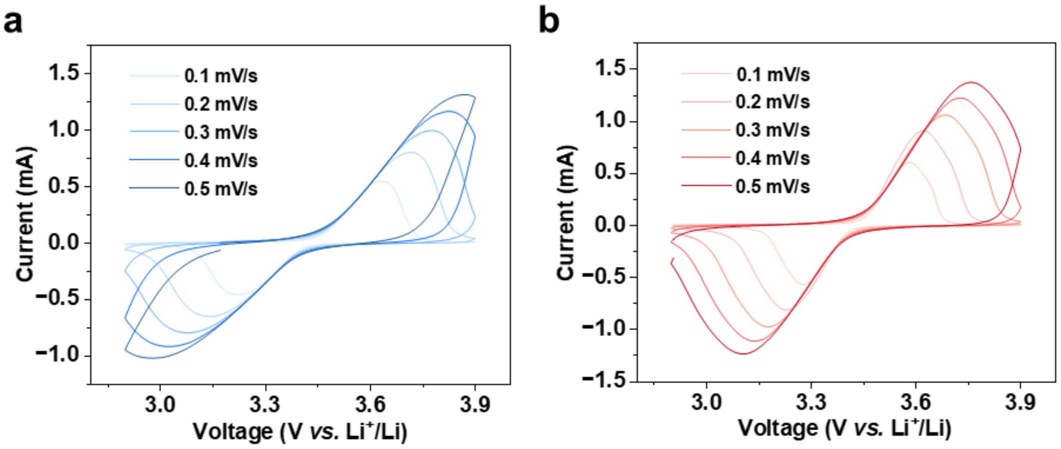

Fig. S9 The CV curves of S-LFP (a) and R-LFP-10min (b) at different scanning speeds

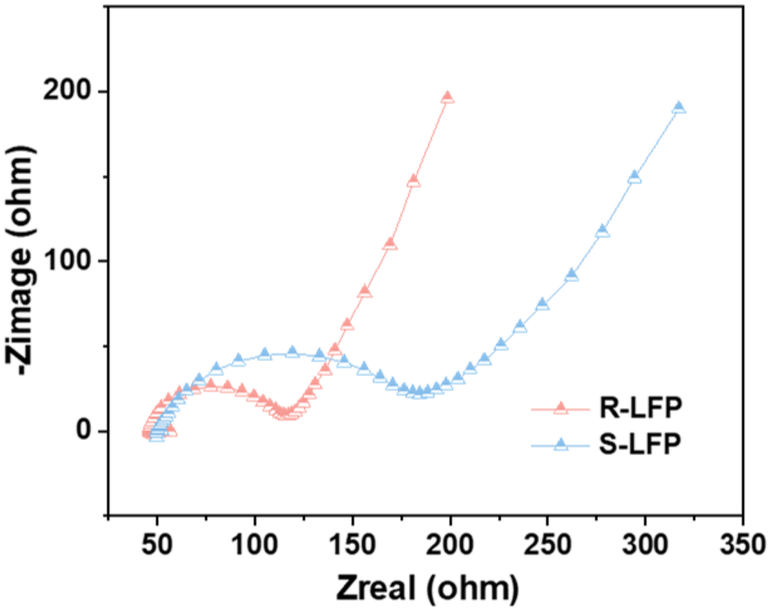

Fig. S10 The EIS curves of S-LFP and R-LFP-10min.

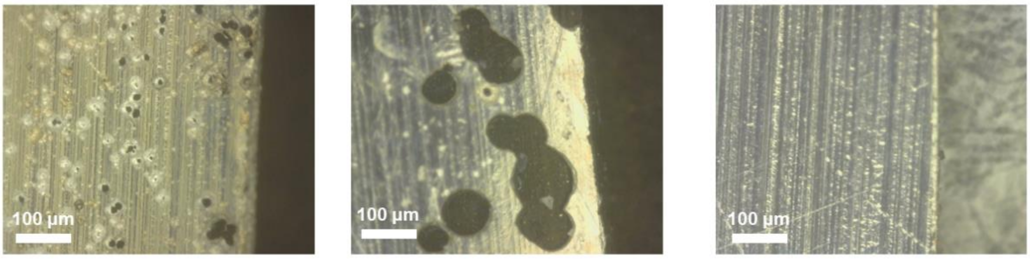

Fig. S11 The morphology of aluminum foil from R-LFP electrodes that were regenerated through immersion in 0.1 M LiI in ethanol, 0.1 M LiI + C_2H_5OLi in ethanol, and 0.1 M LiI + 0.1 M $LiNO_3$ in ethanol for 10 min. (left to right)

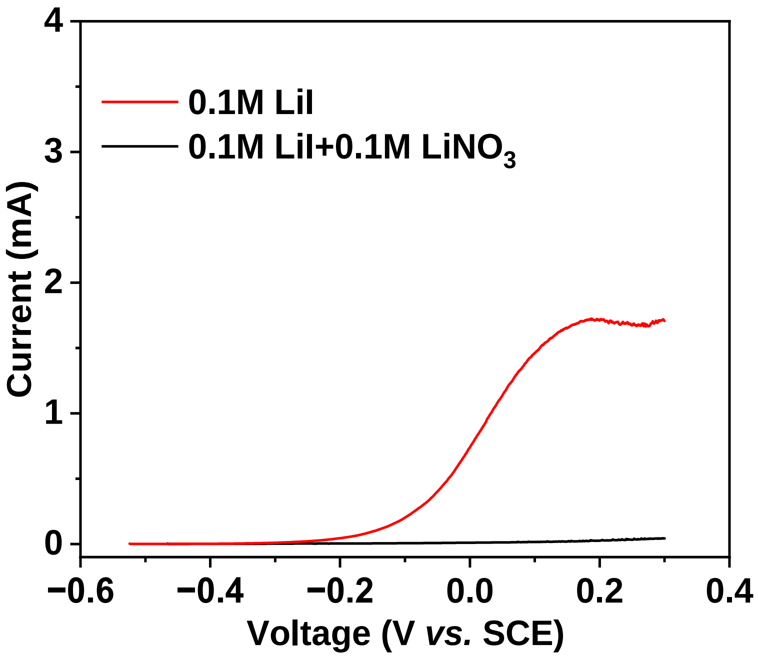

Figure S12. The LSV profile of 0.1M LiI and 0.1M LiI + 0.1M LiNO$_3$ ethanol solution.

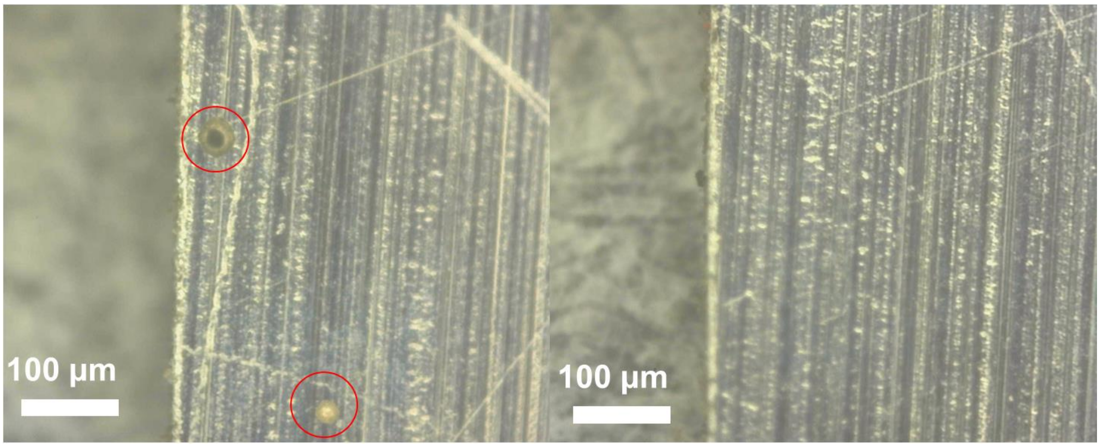

Figure S13. The morphology of aluminum foil after LSV tests that were immersed in 0.1 M LiI (left) and 0.1 M LiI + 0.1 M $LiNO_3$ (right) ethanol solution.

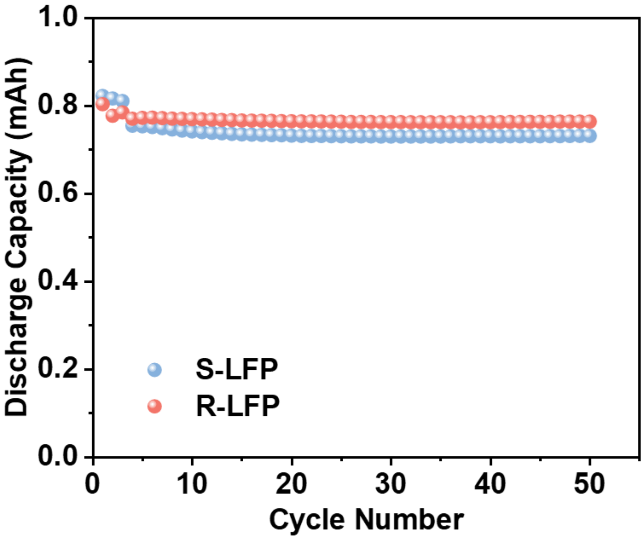

Fig. S14 The cycle performance of the S-LFP electrode and the regenerated electrode

Section S3. Supplementary Tables

Table S1 Structural parameters obtained from Rietveld refinement of the X-ray diffraction pattern of S-LFP. Phase $LiFePO_4$: Space group: Pnma, a = 10.32823 Å, b = 6.00687 Å, c = 4.69310 Å, V = 291.161 Å^3, $\alpha = \beta = \gamma = 90°$. Phase $FePO_4$: Space group: Pnma, a = 9.81996 Å, b =5.79049 Å, c = 4.78393 Å, V = 272.025 Å^3, $\alpha = \beta = \gamma = 90°$.

$LiFePO_4$ (Space Group Pnma) Phase Ratio: 89.8%				
Lattice Parameters	***a* / Å**	***b* / Å**	***c* / Å**	**V / Å^3**
	10.314(4)	5.998(5)	4.698(3)	290.66(4)
Li/Fe Antisite	4.60%			
$FePO_4$ (Space Group Pnma) Phase Ratio: 10.2%				
Lattice Parameters	***a* / Å**	***b* / Å**	***c* / Å**	**V / Å^3**
	9.837(3)	5.795(5)	4.787(1)	272.86(3)
Agreement Factors				
	R_{wp} 3.60%		**χ^2** 1.06%	

Table S2 Structural parameters obtained from Rietveld refinement of the X-ray diffraction pattern of R-LFP-10min. Phase LiFePO$_4$: Space group: Pnma, a = 10.32823 Å, b = 6.00687 Å, c = 4.69310 Å, V = 291.161 Å^3, $\alpha = \beta = \gamma = 90°$.

LiFePO$_4$ (Space Group Pnma) Phase Ratio: 100%				
Lattice Parameters	***a* / Å**	***b* / Å**	***c* / Å**	**V / Å^3**
	10.316(2)	6.000(1)	4.695(5)	290.58(3)
Li/Fe Antisite	1.13%			
Agreement Factors				
	R$_{wp}$	3.68%	χ^2	1.14%

Table S3. Comparison of Different Methods for LFP Recycling by Everbatt Model

Method	Operation Temperature	Processing Time	Lithiation Efficiency	Energy Consumption (kWh/kg LFP)
This Work (Iodide/Triiodide Redox Mediator)	Room Temp (~25°C)	10 minutes	~95–100%	<1
Electrochemical Method (Ref. 1)	Room Temp (~25°C)	>30 minutes	~95–100%	~5
Chemical Leaching (Ref. 2)	Room Temp to Heated	>1 hour	~95–100%	~2–4
High-Temperature Calcination (Ref. 3)	>500°C	2–4 hours	~90–95%	~15–20
Traditional Pyrometallurgical Recycling	>1000°C	Several hours	~90–95%	~15–20
Hydrometallurgical Recycling	Room Temp to Heated	Several hours to days	~85–95%	~5–10