Supporting Information for

# One-step regeneration and upgrading of spent LiFePO$_4$ cathodes with phytic acid

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**Experimental Section**

Materials: The spent 18650-type LIBs were purchased from a local electronic market in Xuzhou, Jiangsu Province, China. To obtain cathode material, the spent LIBs were discharged in a 5 wt.% NaCl solution for 24 h. Then the Al foils and cathode material were separated by manual disassembly.

Regeneration of cathode materials: For hydrothermal treatment, phytic acid (25 mg) and LiOH (5 mg) were added to a 50 mL Teflon liner autoclave filled with 10 mL of water, and 100 mg spent cathode powder were added after stirring for 2 h. The autoclave was heated at 200 °C for 5 h. The treated powders were centrifuged, collected, vacuum drying at 120 °C for 12 h.

Coin cell assembly: The samples (S-LFP, C-LFP, and R-LFP-LP) were mixed with PVDF and carbon black in NMP at a mass ratio of 8:1:1. Then, the slurries were coated on Al foil and dried in vacuum at 120 °C for 12 h. Coin cells (2032) were assembled with a Li metal disc (thickness 450 μm) as the anode, 1 M LiPF6 in EC:DEC:DMC (1:1:1 Vol%) as the electrolyte, and a Celgard 2400 membrane as the separator.

Material characterization: The concentration of metals was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, PQ9000, Analytik Jena AG, German). The morphology was characterized with scanning electron microscope (SEM, SU8010, Hitachi, Japan). The chemical states of elements were analyzed with X-ray photoelectron spectroscopy (XPS, K-Alpha, ThermoFisher, America). The crystal structure and morphology observation were studied by transmission electron microscopy (FEI, Tecnai F30, USA). The crystalline structure was characterized with X-ray diffraction (XRD, D8 Advance, Bruker, German). Raman analysis was characterized Confocal laser raman spectroscopy (Raman, Xplora Plus, Horiba, France). Carry out the charge and discharge test on the battery test system (Xinwei, China). Electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetry (CV) tests at various scan rates were performed using CHI 760e electrochemical workstation (Chenhua, China).
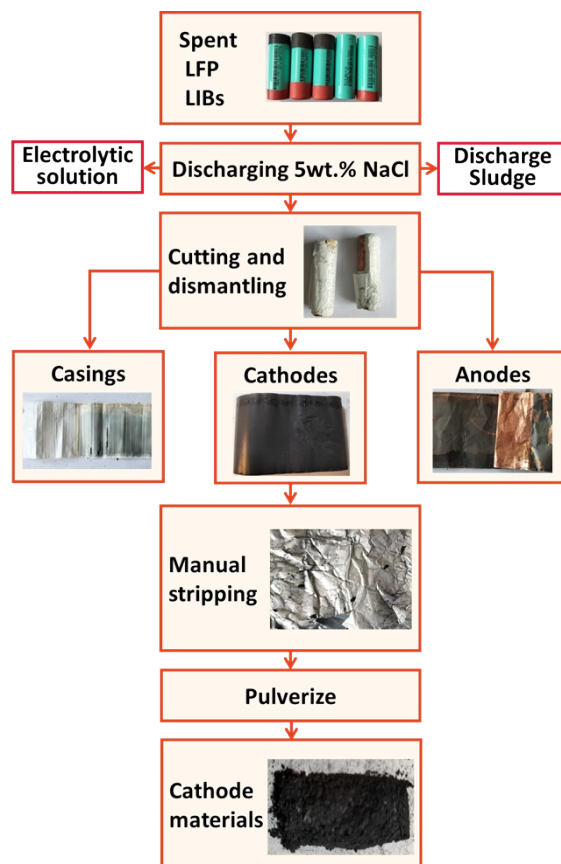
**Supplementary Figures and Tables**



Fig. S1 Flowsheet and digital photos of the recycling cathode materials from spent 18650 type LIBs.
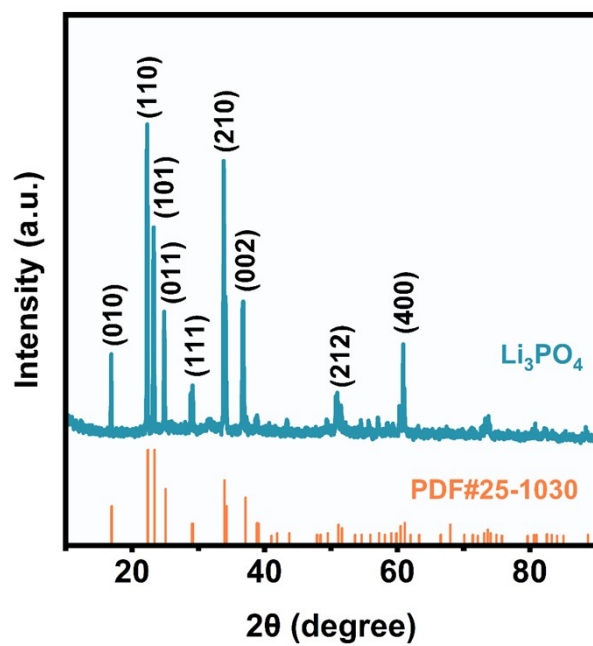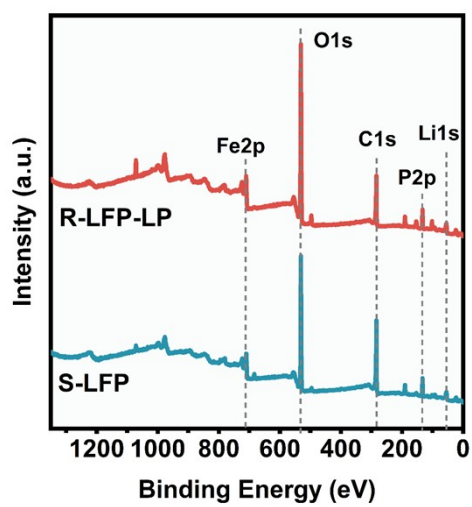
Fig. S2 XRD patterns of Li$_3$PO$_4$.



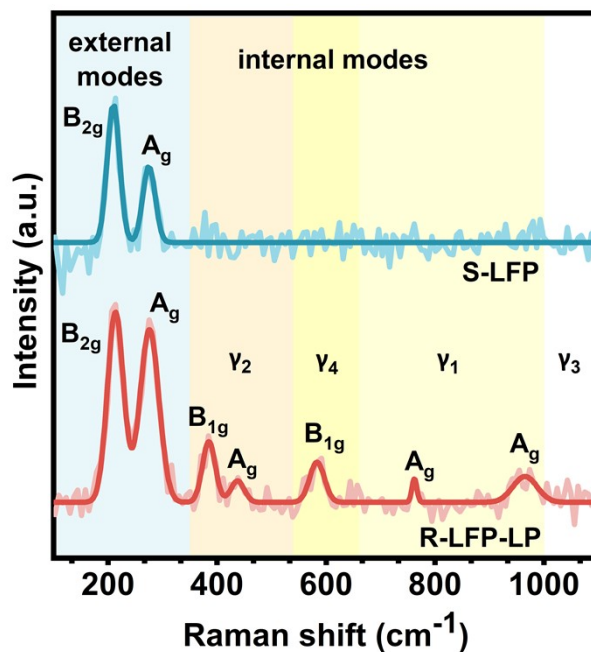Fig. S3 The XPS spectra of S-LFP and R-LFP-LP.

Fig. S4 The Raman spectra of S-LFP and R-LFP-LP.

The vibrational motions of $LiFePO_4$ may be classified into external and internal modes, the external modes which originate in $LiFePO_4$, occur below 350 $cm^{-1}$. They are composed primarily of translatory and rotational motions of the $PO_4^{3-}$ ions and translatory motion of the $Fe^{2+}$ ions.

Among the internal modes in $LiFePO_4$, which are $A1(\nu_1)$ symmetric P-O stretching, $E(\nu_2)$ symmetric O-P-O bond bending, $F1(\nu_3)$ antisymmetric P–O stretching and $F2(\nu_4)$ antisymmetric O-P-O bond bending. The $\nu_2$ mode is a mixture of Li translational and $PO_4$ bending motions of the same symmetry, and strongly coupled with $\nu_4$ modes which involve some Li ion motion.
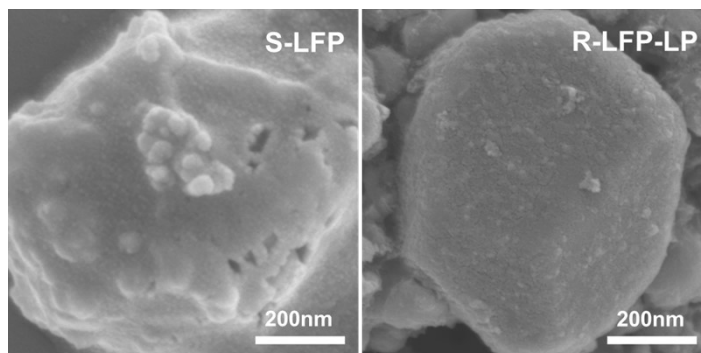


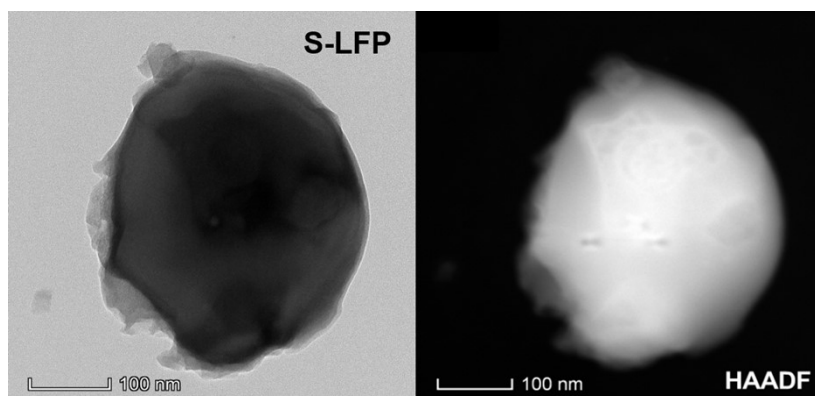Fig. S5 The SEM images of S-LFP and R-LFP-LP.

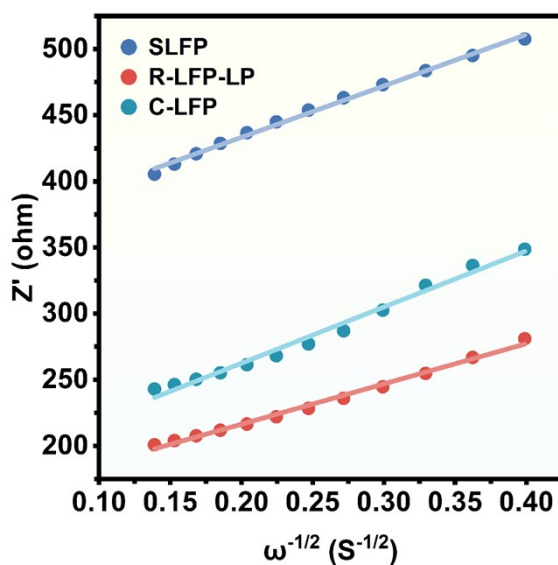Fig. S6 The bright and dark field TEM images of S-LFP.



Fig. S7 Variations and fittings between Z' and the reciprocal square root of the angular frequency ω.

The values of $D_{Li^+}$ are calculated from the inclined lines in the Warburg region using the following equation:

$$D = R^2T^2/2A^2n^4F^4C^2\sigma^2$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode electrode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the $Li^+$ concentration, and σ is the Warburg factor associated with Z' ($Z' \propto \sigma\omega^{-1/2}$). The apparent Li diffusion coefficient D could be calculated from the above equation after linear fitting the relation plot between Z' and

the reciprocal square root of the angular frequency ω to estimate the Warburg factor σ.
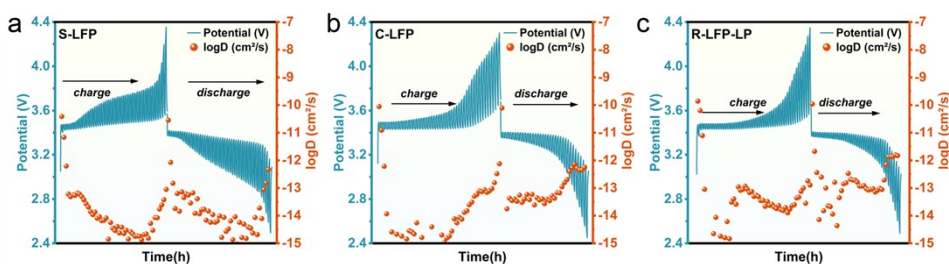


Fig. S8 GITT profiles for the discharge/charge process (blue curves) and diffusion coefficients (red curves) of (a) S-LFP, (b) R-LFP-LP, and (c) C-LFP.

The Li-ion diffusion rate calculated from the GITT curve is based on the following formula according to Fick's second law of diffusion:

$$D = 4/\pi\tau\left(n_M V_M S\right)^2 (\Delta E_S/\Delta E_t)^2$$

where $\tau$ is the duration of the current pulse, $n_M$ is the number of moles, $V_M$ is the molar volume of the electrode, $S$ is the electrode-electrolyte contact area, and $\Delta E_S$ and $\Delta E_t$ are the changes in the steady state potential and the total change during the current flux by deducting the IR drop, respectively. In our experiments, $\tau = 600$ s, $n_M$ = m/M$_{LFP}$, M$_{LFP}$ = 157.76 g mol$^{-1}$, $V_M$ = 20.5 cm$^3$ mol$^{-1}$, $S$ = 1.13 cm$^3$.
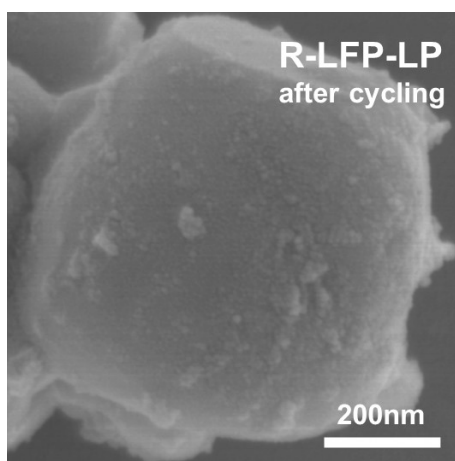


Fig. S9 SEM image of R-LFP-LP after cycling.

**Table S1**. Structural parameters obtained from Rietveld refinement of the X-ray diffraction pattern of S-LFP.

**Phase 1 LiFePO$_4$**: Space group: *Pnma*, Fraction: 91.55%, a = 10.337871Å, b =

6.005399Å, c = 4.692219 Å, α = β = γ = 90°, Lattice volume = 291.307 Å$^3$.

**Phase 2 FePO$_4$**: Space group: *Pnma*, Fraction: 8.45%, a = 5.792714 Å, b = 9.857077 Å, c = 4.768925 Å, α = β = γ = 90°, Lattice volume = 272.302 Å$^3$.

**LiFePO$_4$**

| Atoms | Site | Wyckoff positions | | | Occupancy | U$_{iso}$ |
|:-----:|:----:|:-----:|:-----:|:-----:|:---------:|:----:|
| | | x | y | z | | |
| Li1 | 4a | 0.000000 | 0.000000 | 0.000000 | 0.9390 | 0.1672 |
| Fe2 | 4a | 0.000000 | 0.000000 | 0.000000 | 0.0610 | 0.1672 |
| Fe1 | 4c | 0.291016 | 0.250000 | 0.991829 | 0.9390 | 0.2304 |
| P1 | 4c | 0.094800 | 0.250000 | 0.423000 | 1 | 0.2837 |
| O1 | 4c | 0.126580 | 0.250000 | 1.005501 | 1 | 0.1106 |
| O2 | 4c | 0.445287 | 0.250000 | 0.190920 | 1 | 0.0597 |
| O3 | 8d | 0.383460 | 0.925365 | 0.253612 | 1 | 0.5831 |

**FePO$_4$**

| Atoms | Site | Wyckoff positions | | | Occupancy | U$_{iso}$ |
|:-----:|:----:|:-----:|:-----:|:-----:|:---------:|:----:|
| | | x | y | z | | |
| Fe1 | 4c | 0.275300 | 0.250000 | 0.950400 | 1 | 0.0050 |
| P1 | 4c | 0.093000 | 0.250000 | 0.398900 | 1 | 0.0495 |
| O1 | 4c | 0.115300 | 0.250000 | 0.710700 | 1 | 0.0111 |
| O2 | 4c | 0.445000 | 0.250000 | 0.151100 | 1 | 0.2620 |
| O3 | 8d | 0.164900 | 0.046500 | 0.252000 | 1 | 0.0457 |

**Table S2**. Structural parameters obtained from Rietveld refinement of the X-ray diffraction pattern of R-LFP-LP.

**Phase 1 LiFePO$_4$**: Space group: *Pnma*, Fraction: 89.30%, a = 10.33817 Å, b =

6.008922 Å, c = 4.692074 Å, α = β = γ = 90°, Lattice volume = 291.478 Å$^3$ .

**Phase 2 Li$_3$PO$_4$**: Space group: *Pmn21*, Fraction: 10.70%, a = 6.127176 Å, b = 5.247026 Å, c = 4.883356 Å, α = β = γ = 90°，Lattice volume = 156.997 Å$^3$.

**LiFePO$_4$**

| Atoms | Site | Wyckoff positions | | | Occupancy | U$_{iso}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| | | x | y | z | | |
| Li1 | 4a | 0.000000 | 0.000000 | 0.000000 | 0.9780 | 0.0955 |
| Fe2 | 4a | 0.000000 | 0.000000 | 0.000000 | 0.0220 | 0.0955 |
| Fe1 | 4c | 0.281600 | 0.25000 | 0.975000 | 0.9780 | 0.2598 |
| P1 | 4c | 0.094800 | 0.25000 | 0.423000 | 1 | 0.2837 |
| O1 | 4c | 0.094475 | 0.25000 | 0.775759 | 1 | 0.1106 |
| O2 | 4c | 0.477084 | 0.25000 | 0.313262 | 1 | 0.0597 |
| O3 | 8d | 0.176037 | 0.061147 | 0.135300 | 1 | 0.5831 |

**Li$_3$PO$_4$**

| Atoms | Site | Wyckoff positions | | | Occupancy | U$_{iso}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| | | x | y | z | | |
| Li1 | 4b | 0.377195 | 0.234554 | 0.805672 | 1 | 0.0641 |
| Li2 | 2a | 0.500000 | 0.811474 | 0.942634 | 1 | 0.3457 |
| P1 | 2a | 0.000000 | 0.834319 | 0.031763 | 1 | 0.0303 |
| O1 | 4b | 0.194662 | 0.686552 | 0.866771 | 1 | 0.0494 |
| O2 | 2a | 0.000000 | 0.141240 | 0.908903 | 1 | 0.0491 |
| O3 | 2a | 0.500000 | 0.216175 | 0.867255 | 1 | 0.2856 |