Supplementary Information

A redox targeting-based materials recycling strategy for spent lithium ion batteries

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Experimental section

Materials: Battery grade LiFePO₄ powder was purchased from Li-cell Co. company. Reagent grade LiOH (99.5%), $K_3Fe(CN)_6$ (99.0%), $Fe_4[Fe(CN)_6]_3$ (99.3%) were purchased from Sigma Aldrich without further purification. Nafion 117 membrane (Dupont) was used directly. Solution of $Li_4Fe(CN)_6$ was synthesized by immersing 2.86 g $Fe_4[Fe(CN)_6]_3$ powder into 40 mL 1 M LiOH (0.96 g) solution with deionized water as solvent. After 10 h reaction, 40 mL 0.2 M yellowish $Li_4Fe(CN)_6$ solution was obtained with brown $Fe(OH)_3$ precipitate at the bottom of flask. Solution of 0.20 M $Li_3Fe(CN)_6$ was prepared by electrolyzing $Li_4Fe(CN)_6$ solution. In detail, 40 mL 0.20 M $Li_4Fe(CN)_6$ was pumped through the anodic tank and anodic

compartment of an electrochemical flow cell. A constant current of 5 mA cm⁻² was applied onto the cell to oxidize $Li_4Fe(CN)_6$ to $Li_3Fe(CN)_6$ with a cutoff voltage of 1.2 V. O₂ reduction took place on the counter electrode (cathode) with 0.1 M LiOH solution as the supporting electrolyte. Carbon felt (4 cm²) was used as the anodic and cathodic electrode.

Cyclic voltammetry measurement: LiFePO₄ working electrode was made by coating slurry containing LiFePO₄ powder onto a piece of glassy carbon and dried in a vacuum oven at 80°C. The slurry was prepared by mixing LiFePO₄ powder, carbon black (CB) and polyvinylidene fluoride (PVDF) with N-methyl pyrrolidone (NMP) as solvent (LiFePO₄: CB: PVDF=8: 1: 1). To measure the redox potential of $[Fe(CN)_6]^{4-/}[Fe(CN)_6]^{3-}$, 10 mL 0.20 M Li₃Fe(CN)₆ solution was prepared as electrolyte with glassy carbon as working electrode. Cyclic voltammograms were measured by a three-electrode cell with Pt plate and Ag/AgCl as the counter and reference electrode, respectively. Experiments were conducted with an electrochemical workstation (AUTOLAB PGSTAT30) at a scan rate of 5 mV s⁻¹.

*Chemical reaction of LiFePO*⁴ *with [Fe(CN)*₆*J*³⁻: 40 mL 0.20 M K₃Fe(CN)₆ was used to selectively remove Li⁺ from LiFePO₄. Specifically, 0.5 g LiFePO₄ powder was immersed into a solution of 40 mL 0.20 M K₃Fe(CN)₆ for different time intervals. Residue was collected after the reaction by centrifuge. The crystal structure of the reaction product was characterized by X-ray diffraction (XRD, Bruker D8). Content of Li⁺ in the product was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300DV).

Electrochemical oxygen flow cell tests: An electrochemical flow cell was assembled with two stainless steel end plate, 2×2 cm² graphite felt (from GCL) as anodic and cathodic electrode, and Nafion 117 as membrane to separate anolyte and catholyte. The anolyte was 40 mL 0.20 M Li₄Fe(CN)₆ which was pumped through the anodic tank and cell compartment by a peristaltic pump (Williamson Manufacturing Company Ltd.) at a flow rate of 100 mL min⁻¹. The catholyte was 40 mL 0.1 M LiOH solution, in which O₂ gas was bubbled while the catholyte was pumped into the cathodic compartment. The voltage profile was measured at galvanostatic mode with an Arbin battery testing system at a constant current of 20 mA. The steady-state current density vs. voltage plot was obtained by using staircase potential scan with an Arbin battery testing system. The applied voltage was increased by 0.1 V per step and held for 1 h to ensure that the cell has reached a steady state.

 Li^+ concentration in catholyte was measured by ICP-OES. An oxygen flow cell with 40 mL 0.25 M $Li_4Fe(CN)_6$ anolyte and 40 mL 0.1 M LiOH catholyte was assembled. O₂ gas was bubbled and pumped into cathodic compartment with the catholyte. A constant current of 20 mA was applied. 0.5 mL catholyte was taken out with a time interval of 1 h during the experiment, from which the amount of Li^+ was detected by ICP-OES measurement.

Demonstration of redox targeting-based LiFePO₄ recycling: Homemade LiFePO₄ flakes were firstly made to simulate the recycling of spent material. Slurry of LiFePO₄ was firstly prepared by mixing the powder with carbon back (CB) and polyvinylidene fluoride (PVDF) with N-methyl pyrrolidone (NMP) as solvent (LiFePO₄: CB: PVDF=8: 1: 1). The slurry was then

coated onto aluminum foil and dried in a vacuum oven at 80 °C for 12 h. After that, LiFePO₄ flakes were scraped off from the aluminum foil for subsequent use. 0.90 g LiFePO₄ flakes were loaded into the anodic tank containing 40 mL 0.20 M Li₃Fe(CN)₆ solution, which was pumped through the tank and anodic compartment of the cell. In the cathodic tank, O₂ was bubbled into 30 mL 0.1 M LiOH catholyte which was pumped through the cathodic compartment. Carbon felt (2×2 cm² in area) was used as the electrodes. The reaction was carried out at a constant current of 20 mA with a cutoff voltage of 1.2 V. After the experiment, water in the catholyte was evaporated in a vacuum oven at 80 °C to get LiOH. Fourier transform infrared (FTIR) spectroscopy with ATR mode (Perkin-Elmer) was used to characterize the obtained LiOH sample.

OCP measurement: 40 mL 0.20 M K₃Fe(CN)₆ solution was prepared and stored in a flask as shown in Figure S2. Potentiometry was conducted with glassy carbon and Ag/AgCl as the working and reference electrode respectively, to monitor the equilibrium potential of $[Fe(CN)_6]^4$ -/ $[Fe(CN)_6]^3$ - by measuring the open circuit potential (OCP) of the solution. 4 g LiFePO₄ was added into the solution and the changes of OCP were recorded with an electrochemical workstation (AUTOLAB PGSTAT30).

Determination of reaction rate constant: The concentration of generated $K_4Fe(CN)_6$ was calculated based on the Nernst equation:

$$E = E^0 - \frac{RT}{F} \ln \frac{c}{0.2 - c}$$
 (S1)

Here *E* is the OCP of K₃Fe(CN)₆ solution upon reacting with LiFePO₄, *E⁰* is the standard potential (0.37 V vs. SHE), *c* is the concentration of K₄Fe(CN)₆. The reaction rate constant (k^0) and electron transfer coefficient (α) between LiFePO₄ and K₃Fe(CN)₆ were determined in terms of the Butler–Volmer equation (S2).

$$\frac{i}{AF} = k^0 \left[c e^{-\alpha \frac{F}{RT}(E - E^0)} - (0.2 - c) e^{(1 - \alpha) \frac{F}{RT}(E - E^0)} \right]$$
(S2)

Here *i* is the current, *A* is the area of electrode, *F* is the Faradaic constant, *R* is the universal gas constant, *T* is the temperature. Here the flux of electron transfer from LiFePO₄ to $[Fe(CN)_6]^{3-}$ is equivalent to the *i* detected by electrode. Therefore, *i* could be replaced by the concentration change of $[Fe(CN)_6]^{3-}$ as the equation (S3).

$$i = VF\frac{dc}{dt}$$
(S3)

Here V is the volume of $[Fe(CN)_6]^{3-}$ solution, 40 mL. Combining eq.(S1), eq.(S2) and eq.(S3)

obtains the reaction rate \overline{dt} ,

dc

$$\frac{dc}{dt} = k^0 c e^{(1-\alpha)(0.1+0.0257\log\left(\frac{c}{0.2-c}\right))/0.0257}$$
(S4)

 k^0 and α were determined to be 0.455 A g⁻¹ and 0.80 by fitting the OCP vs. reaction flux curve with MATLAB software. Note that k^0 was not scaled to the surface area of material and volume of solution.





Supplementary Fig. S1. Fourier transform infrared (FTIR) spectra of LiFePO₄ before and after

reacting with 0.25 M K₃Fe(CN)₆ solution.



Supplementary Fig. S2. Photo of the three-electrode cell used to monitor the open circuit

potential (OCP) of 40 mL 0.2 M K₃Fe(CN)₆ during the reaction with 4.0 g LiFePO₄.



Supplementary Fig. S3. Linear sweep voltammetry (LSV) plot of 40 mL 0.2 M $K_3Fe(CN)_6$ after reacting with 4.0 g LiFePO₄. The experiment was conducted with a rotating disc electrode at a rotation rate of 1000 RPM. The counter electrode was a platinum plate, and the scanning rate was 10 mV s⁻¹.



Supplementary Fig. S4. Steady-state current density of the oxygen flow cell obtained at different applied voltage. The staircase voltage increase was controlled with an Arbin battery



tester. The time interval was 1 h for each step to reach a steady state.

Supplementary Fig. S5. Cyclic voltammograms of carbon felt with and without O_2 gas bubbled into the electrolyte. The electrolyte was 0.1 M LiOH solution. The counter electrode was a platinum plate. The scan rate was 10 mV s⁻¹.



Supplementary Fig. S6. Setup of the oxygen flow cell for regenerative redox targeting-based

LiFePO₄ recycling.



[Fe(CN)₆]⁴⁻

[Fe(CN)₆]³⁻

Pump

Supplementary Fig. S7. Synthesis process of $Li_3Fe(CN)_6$ from the reaction of Prussian blue in LiOH solution and electrolysis of $Li_4Fe(CN)_6$.

0

0 02

Pump



Supplementary Fig. S8. Cyclic voltammograms of 0.20 M $Li_3Fe(CN)_6$ solution synthesized from Prussian blue and LiOH. The working electrode was glassy carbon, and the counter electrode was a platinum plate.



Supplementary Fig. S9. X-ray diffraction pattern of LiOH obtained from the catholyte and the comparison with a commercial anhydrate LiOH.