Supporting Information

Co-recovery of spent $LiCoO_2$ and $LiFePO_4$ by paired electrolysis

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Number of pages: 21

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Number of tables: 5

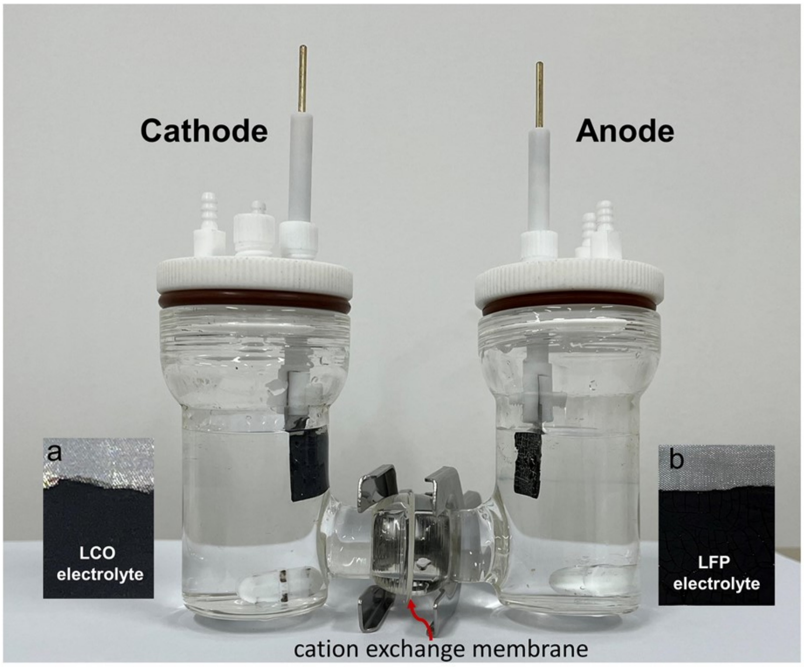

Fig. S1 Digital photos of the homemade LCO and LFP electrodes and the H-type electrolyzer.

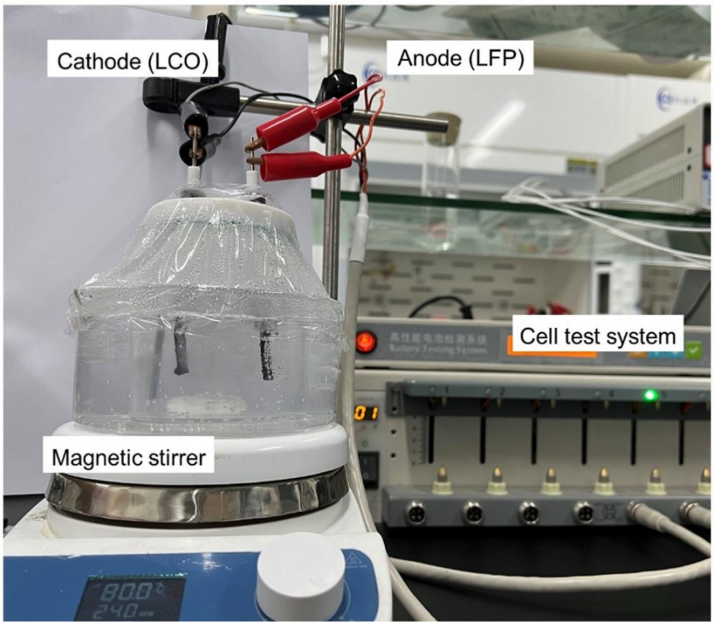

Fig. S2 Schematic diagram of the electrolysis unit

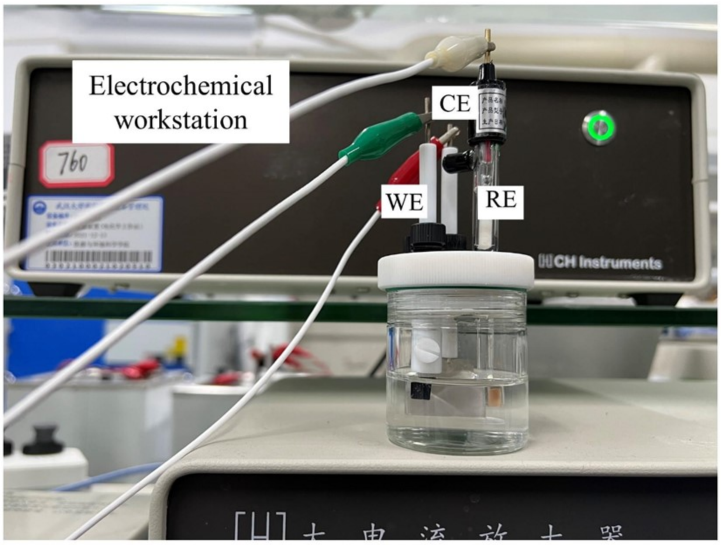

Fig. S3 Schematic diagram of the electrochemical workstation

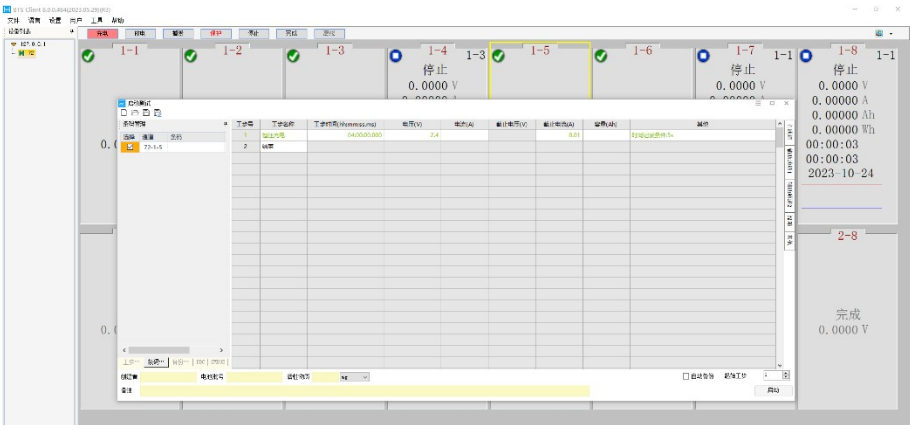

Fig. S4 Programming of the cell test system

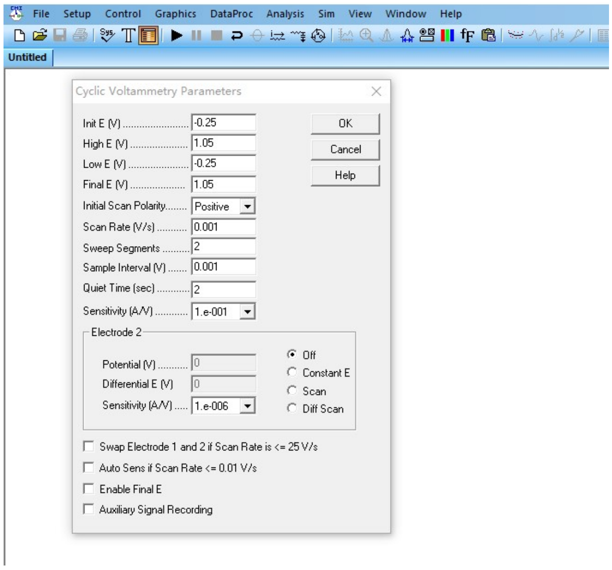

Fig. S5 Programming the electrochemical workstation for cyclic voltammetry testing of LFP

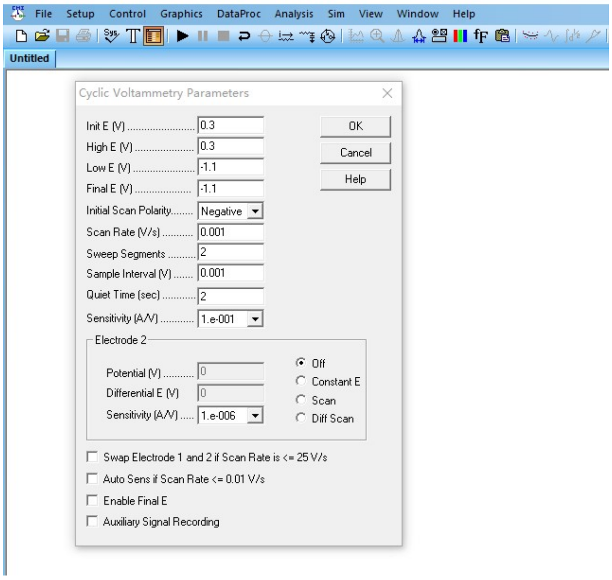

Fig. S6 Programming the electrochemical workstation for cyclic voltammetry testing of LCO

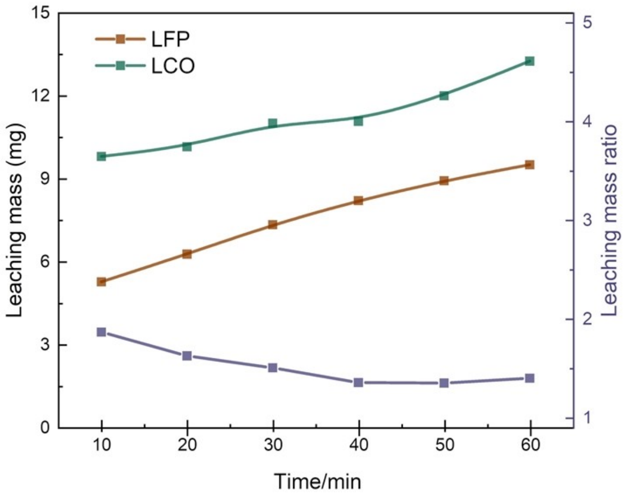

Fig. S7 Leaching mass and leaching mass ratio of Li of LCO and LFP in two independent chambers.

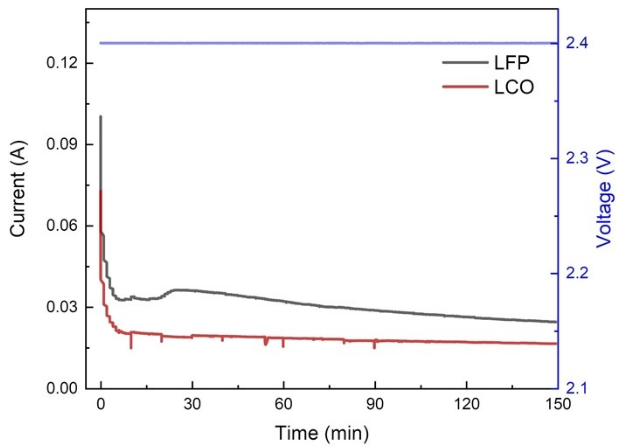

Fig. S8 Current curves of the LCO electrode and LFP electrode at the same conditions in two independent systems.

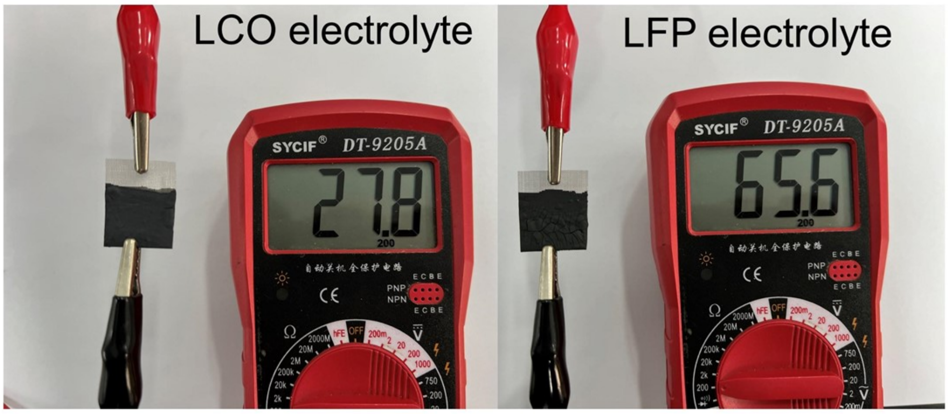

Fig. S9 Resistance of the homemade LCO electrode and the LFP electrode.

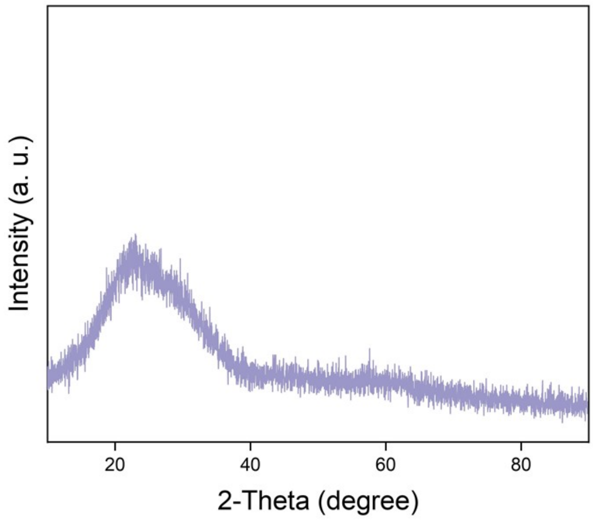

Fig. S10 XRD pattern of the precipitation in the electrolyte at 80 ℃, 0.03 M H_2SO_4 solution, 240 min.

Economic and Environmental Analysis

The EverBatt model, a closed-loop battery recycling model developed at Argonne National Laboratory, was used to conduct a techno-economic and life-cycle analysis of pyrometallurgical, hydrometallurgical, and the direct electrochemical reduction processes. Our analysis was focused on the total energy use and GHG emissions of the three recycling methods and did not include the emissions or energy associated with their use in electric vehicles.

Pyrometallurgy (Fig. S11) and hydrometallurgy (Fig. S12) are used as end-of-life battery treatment options. Although their entire process may not apply to $LiFePO_4$ recovery, especially in the Ni and Co recovery step. In the current industry, pyrometallurgy and hydrometallurgy processes do not sort spent batteries before recycling. Therefore, as assumed in this study, regardless of the cathode composition of the spent battery, it will go through the same recycling process.

In this study, EverBatt's generic direct recovery process is modified to describe the direct electrochemical oxidation process. As shown in Fig. S13, the material undergoes a series of physical separation processes to separate the scrap metal, plastic, and black powder. After that, the collected black powder is worked as the electrolytic anode in Na_2CO_3 solution for the process of de-lithiation to recover Li_2CO_3 and $FePO_4$.

It is worth noting that the commercial pyrometallurgical flow chart and commercial hydrometallurgical flow chart here are obtained from Everbatt 2020 and are copied here for readers to understand.[1]

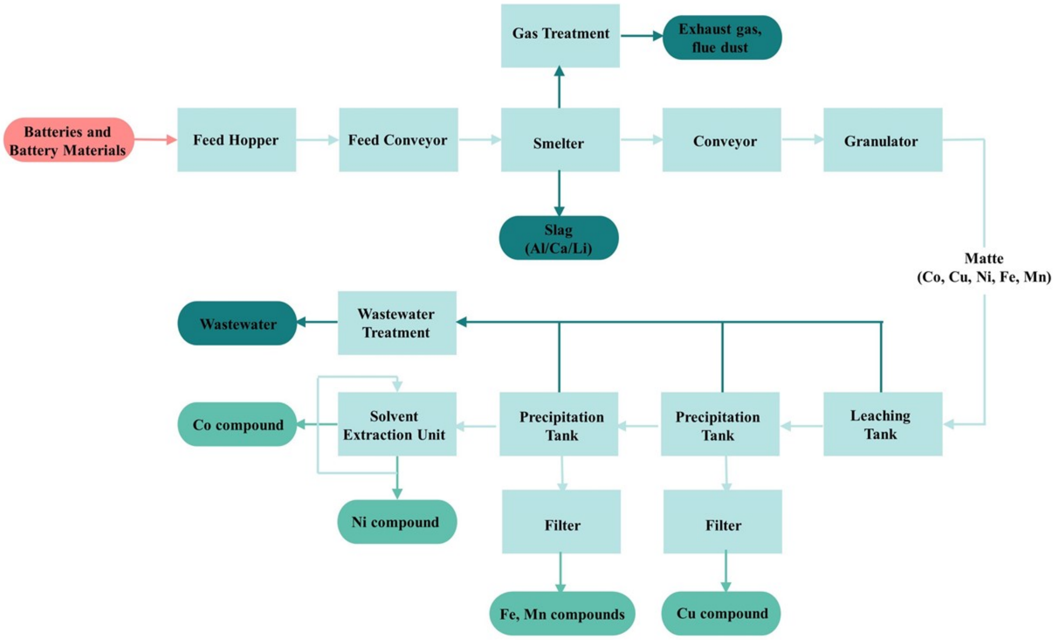

Fig. S11. Process diagram of a pyrometallurgical process.

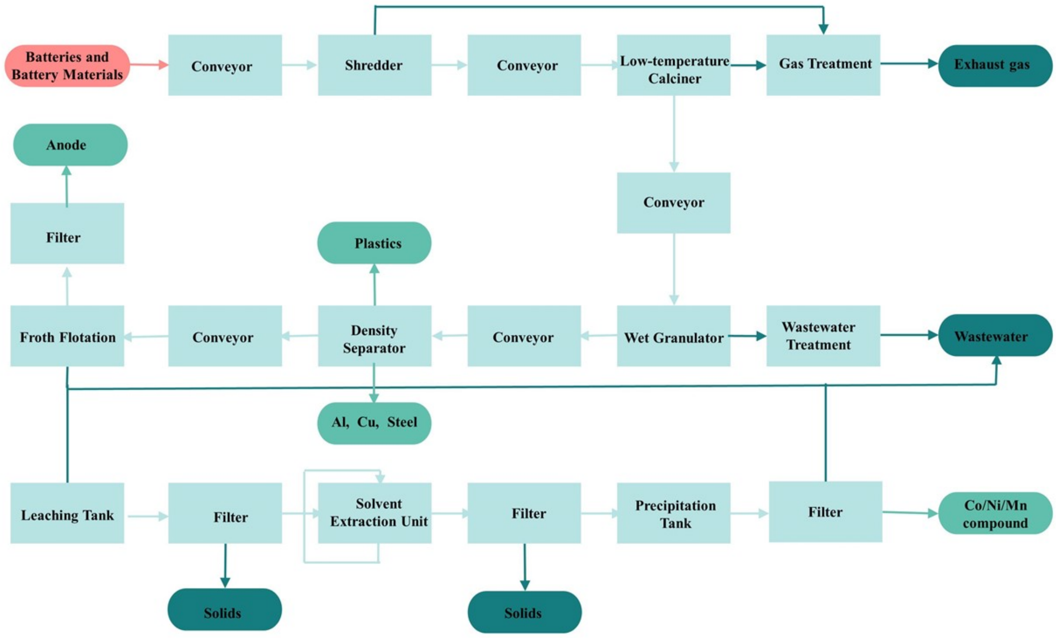

Fig. S12. Process diagram of a hydrometallurgical process.

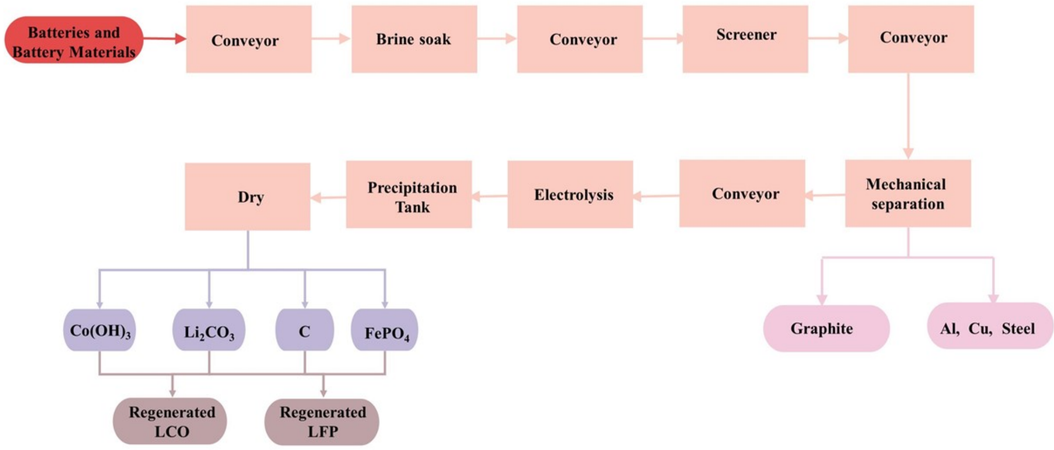

Fig. S13. Process diagram of an electrometallurgical process.

Tab. S1. Kinetic parameters of Li and Co of LCO at 2.4 V, in 0.03 M H_2SO_4 solution.

Temperature	Surface chemical reaction (Li)		Surface chemical reaction (Co)	
(^oC)	K (min^{-1})	R^2	K (min^{-1})	R^2
40	0.00276	0.99236	0.00223	0.99632
50	0.00301	0.99314	0.00214	0.99158
60	0.00566	0.99908	0.00498	0.9979
70	0.00631	0.99796	0.00601	0.99553
80	0.00704	0.99773	0.00753	0.99836

Tab. S2. Kinetic parameters of Li of LFP battery at 2.4 V, in 0.03 M H_2SO_4 solution.

Temperature (°C)	Surface chemical reaction	
	K (min^{-1})	R^2
40	0.00851	0.99903
50	0.00982	0.99875
60	0.01186	0.998959
70	0.014	0.99927
80	0.01608	0.99465

Tab. S3. Ea values of Li and Co for LCO and Li for LFP at 2.4 V, in 0.5 M Na_2CO_3 solution.

Types	Li for LCO	Co for LCO	Li for LFP
Ea (kJ/mol)	23.378	28.703	14.945
R^2	0.99401	0.9939	0.99866

Table S4. Materials requirements (kg) to recycle 1 kg of spent batteries through different recycling technologies.

Pyrometallurgy	Hydrometallurgy	Electrolysis
Hydrochloric acid	Ammonium hydroxide	Soda Ash
Hydrogen peroxide	Hydrochloric acid	
Limestone	Hydrogen peroxide	
Sand	Sodium hydroxide	
	Sulfuric acid	
	Soda ash	

Table S5. Value of recycled materials ($/kg)

	Pyrometallurgy	Hydrometallurgy	Electrolysis
Copper	0.91	0.91	0.91
Aluminum		0.13	0.13
Graphite		0.08	0.04
Co^{2+} in products	12.38	12.38	
LCO			18.16
LFP			5.5

Reference:

1. Q. Dai, J. Spangenberger, S. Ahmed, L. Gaines, J. Kelly and M. Wang, *Argonne National Laboratory*, 2019.