Supplementary information

Organophosphonic acids-assisted efficient delamination of spent lithium-ion battery cathodes for regeneration

Cheng Gong[a,b], Shiwen Zhang[a,b*], Qin Liu[c], Jia Yi[b], Wentuan Bi[a,b*]

a. School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, P. R. China.

b. Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui, 230031, P. R. China.

c. Key Laboratory of Precision and Intelligent Chemistry, University of Science and Technology of China, Hefei, 230026, P. R. China.

† To whom correspondence should be addressed: E-mail: bwin@ustc.edu.cn, shwzhang@aust.edu.cn.

Experimental Section

Materials and reagents

The spent $LiNi_{0.55}Co_{0.15}Mn_{0.3}O_2$(Ni55) LIBs were purchased from Li-Fun Technology Co., Ltd. The spent batteries were discharged to 2.0 V using a Neware battery testing system and then manually disassembled to obtain Ni55 cathode sheets, which were dried overnight at 60°C for further processing. All the chemical reagents used in this study are of analytical grade and purchased from Aladdin Reagent Co. Ltd.

Experimental process

Firstly, the Ni55 cathode sheets were cut into 0.5×0.5 cm² pieces and then placed in the organophosphonic acids aqueous solution at 25°C, with a liquid-to-solid ratio at 1:50 (L/g), until the cathode materials were completely separated from the Al foil. The initial pH of the PBTCA aqueous solution was 0.74 and it was tuned using concentrated hydrochloric acid or ammonia. The collected solution was used for metal leaching rate measurement, while the separated cathode materials and Al foils were rinsed three times with deionized water and then dried overnight at 60°C for subsequent characterization. 1,2-ethylenediphosphonic acid (EDPA), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), 3-phosphonopropionic acid (PPA), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl) were evaluated under the same condition for comparison. The metal leaching rate was calculated using the following formula:

$$\mu = \frac{c \times V}{m \times wt\%}$$

Where μ is the metal leaching rate, c is the concentration of ions in the separation solution (g·L^{-1}), V is the volume of the separation solution (L), m is the weight of the cathode sheet (g), and wt% is the weight percentage of different metals in the cathode sheet.

Cathode material regeneration

The separated Ni55 cathode materials were ground into powder and mixed with LiOH·H$_2$O at a molar ratio of Li:(Ni+Co+Mn)=1.10:1. It was then heated in a muffle furnace at 300°C for 2 hours and 750°C for 8 hours with a heating rate of 5°C/min, yielding regenerated Ni55 cathode materials.

Material characterization

The components of the separated Ni55 cathode material and the metal content in the solution were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP PRO). The morphology and structure of the materials were characterized using X-ray diffraction (XRD, MiniFlex 600), scanning electron microscopy (SEM, SUPRATM 40), and transmission electron microscopy (TEM, JEM-2100). The surface element composition of the separated Al foil was analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis supra+).

Electrochemical characterization

The cathode was prepared by mixing the active cathode materials, conductive carbon, and PVDF with a mass ratio of 8:1:1 using NMP as the solvent. The as-prepared slurry was coated onto the cleaned Al foil and then vacuum-dried at 80°C for 12 hours. After drying, the cathode sheet was cut into discs with a diameter of 12

mm. The CR2032 button cells were assembled using pure lithium foil as the anode, 1 M LiPF$_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DEC) with a volume ratio of 1:1 as the electrolyte, and Celgard 2400 as the separator. The electrochemical performance tests were conducted using a Neware battery testing system. The first charge-discharge tests were carried out at a voltage range of 2.8 to 4.3 V at a rate of 0.1 C. The cycling performance was tested at 0.3 C after 5 cycles at 0.1 C. The rate performance tests were carried out at 0.3 C, 0.5 C, 1.0 C, and 2.0 C after 3 cycles at 0.1 C. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted using an electrochemical workstation (Biologic VMP-3e). The CV tests were carried out at the voltage range of 2.8 to 4.3 V with a scan rate of 0.1 mV·s^{-1}. The EIS tests were conducted over a frequency range of 100 kHz to 100 mHz with an amplitude of 10 mV.

Economic and environmental analysis

The economic and environmental analysis was conducted using the EverBatt model developed by Argonne National Laboratory. After the basic parameters such as plant information, feedstock composition were entered, its built-in computational framework was employed to assess the economic benefits (e.g., costs and revenues) and environmental impacts (e.g., energy consumption, CO_2 emissions, and water usage) of the PBTCA-based process. Additionally, a comparative analysis was conducted against pyrometallurgical (Pyro), hydrometallurgical (Hydro), and direct (Direct) methods.
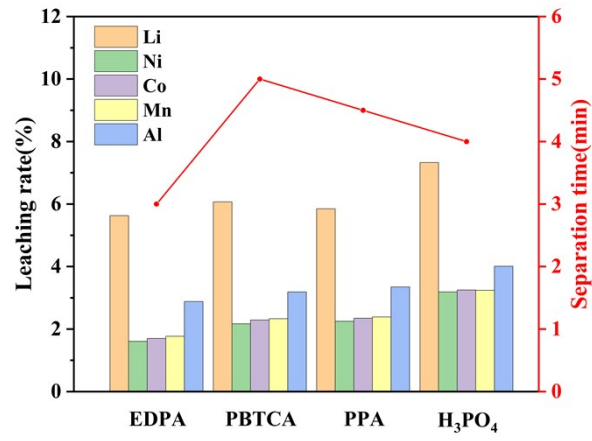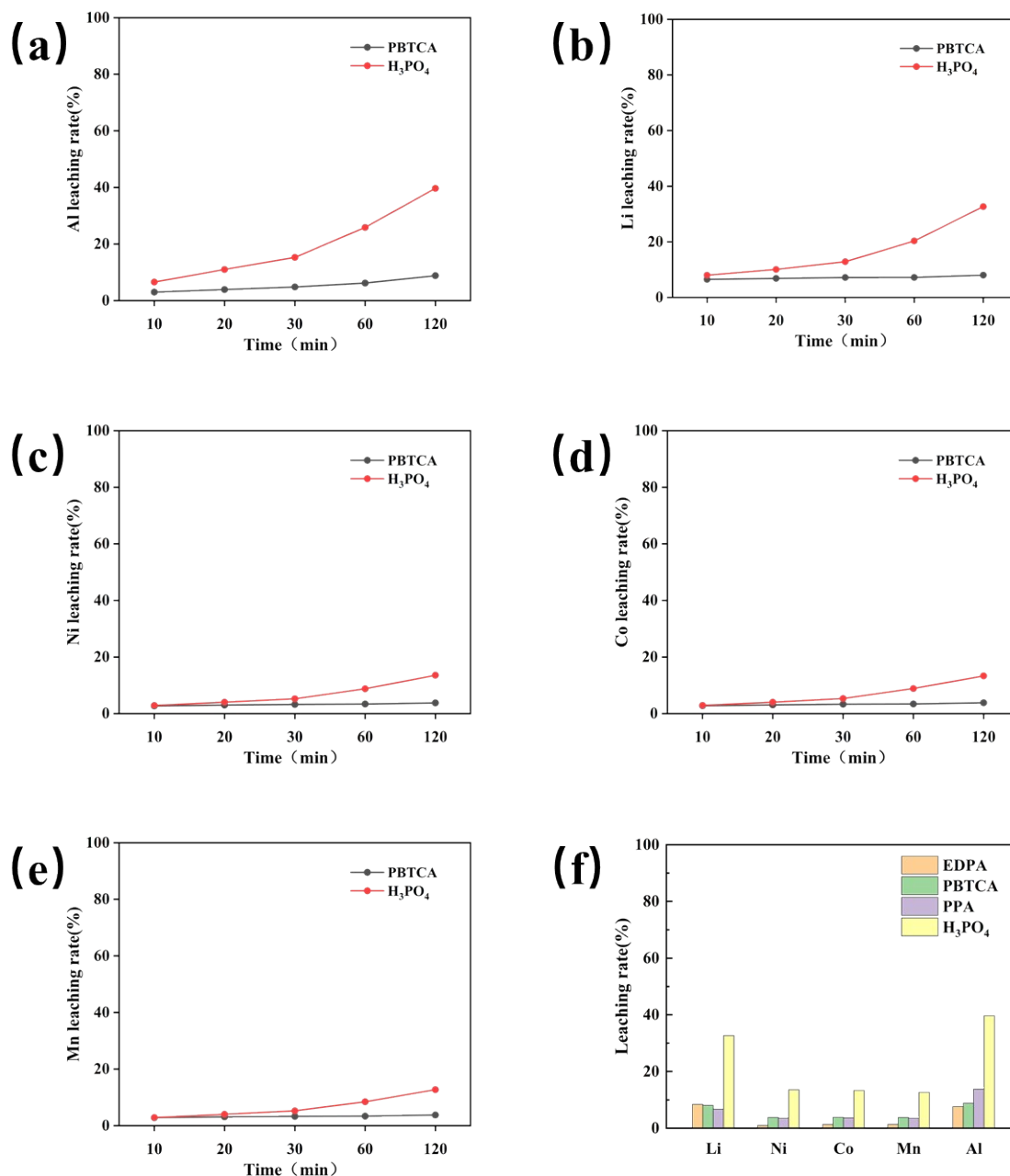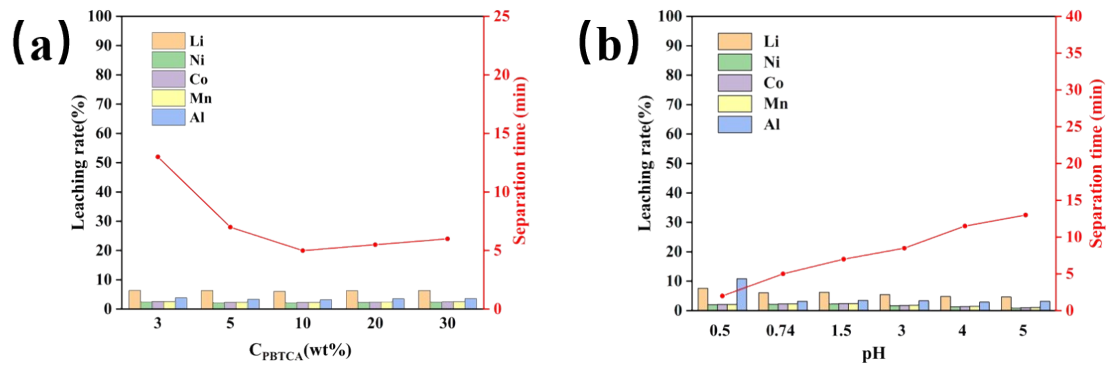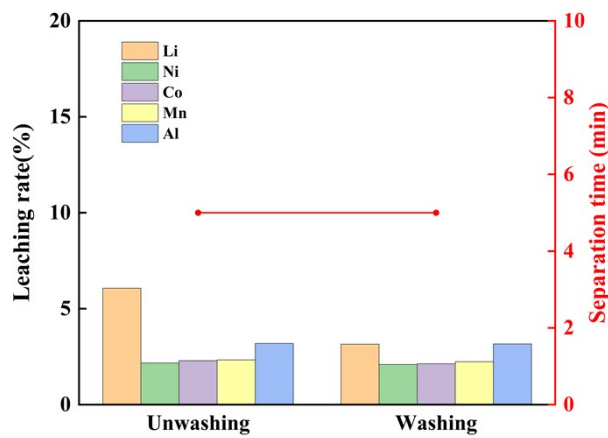
Fig. S1. Leaching rates of Li, Ni, Co, Mn, and Al and the separation time using organophosphonic acids and H_3PO_4.

Fig. S2. Time-dependent leaching rates of (a) Al (b) Li (c) Ni (d) Co and (e) Mn in PBTCA and H_3PO_4. (f) Leaching rates of Li, Ni, Co, Mn, and Al in organophosphonic acids and H_3PO_4 after 120 minutes.

Fig. S3. (a) Effect of PBTCA solution concentration on leaching rates of Al, Li, Ni, Co, and Mn. (b) Effect of pH on leaching rates of Al, Li, Ni, Co, and Mn ($C_{PBTCA} = 10$ wt%).

Fig. S4. The separation time and the leaching rates of Li, Ni, Co, Mn, and Al using 10 wt% PBTCA solution for the Ni55 cathode sheets before and after rinsing with deionized water.
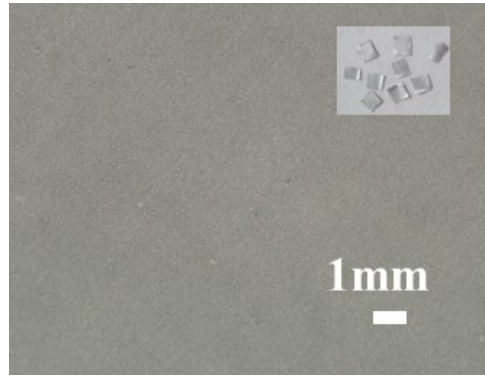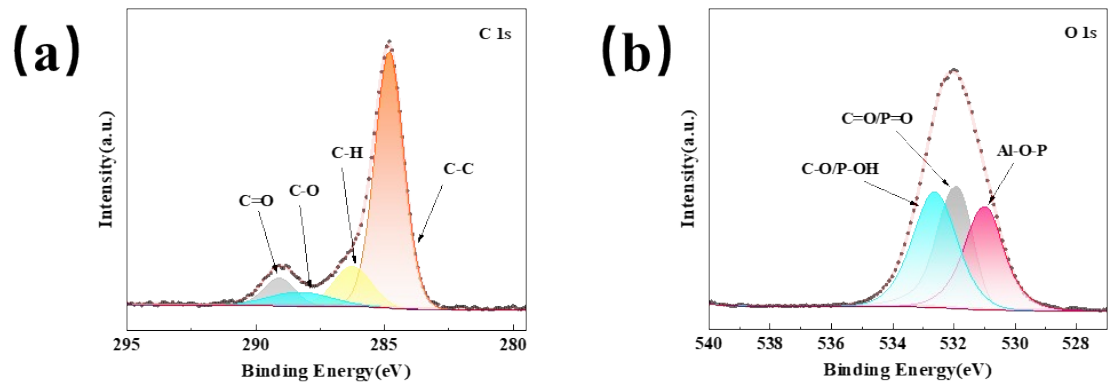
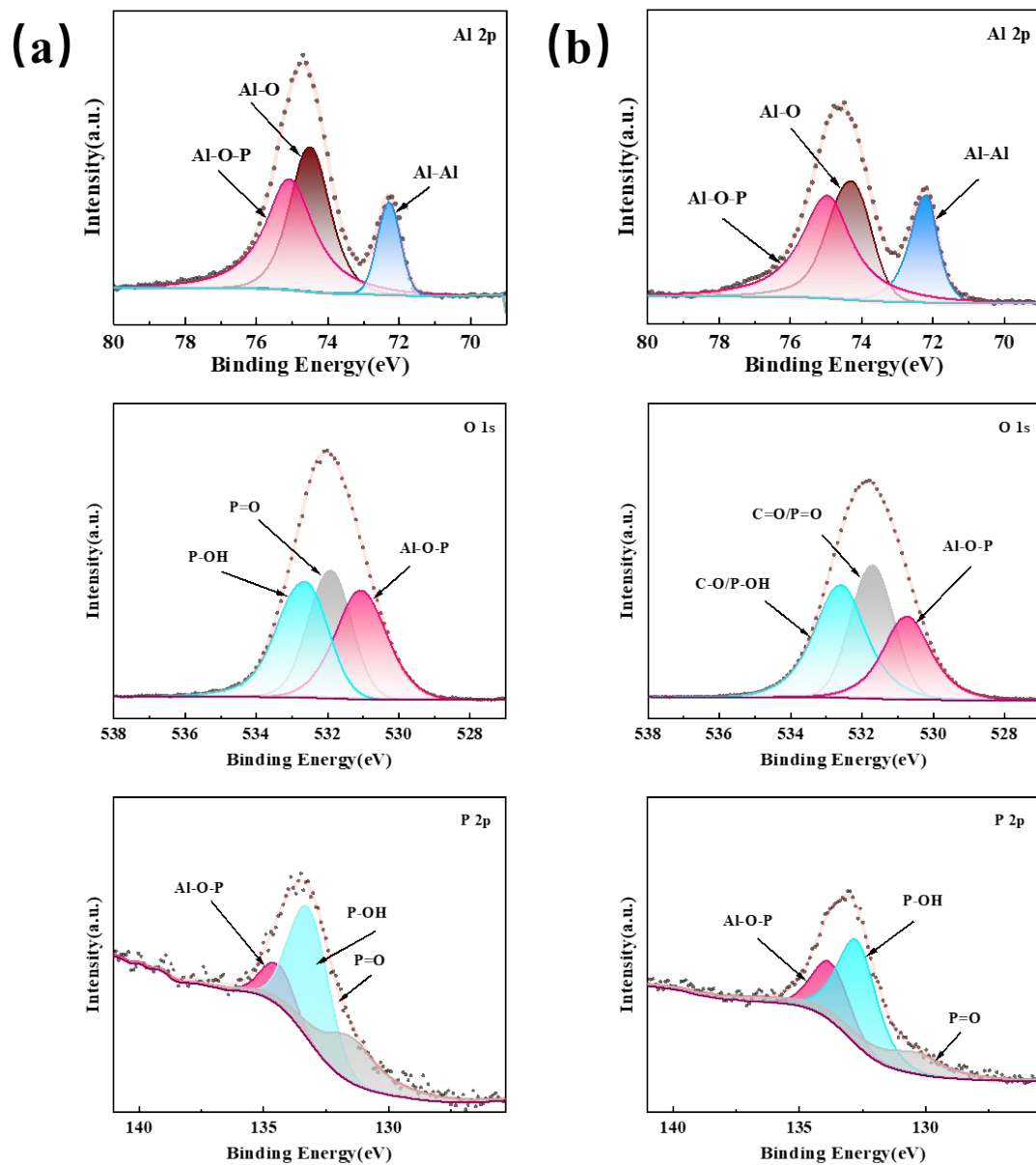**Fig. S5.** Optical microscopy image of the separated Al foil.
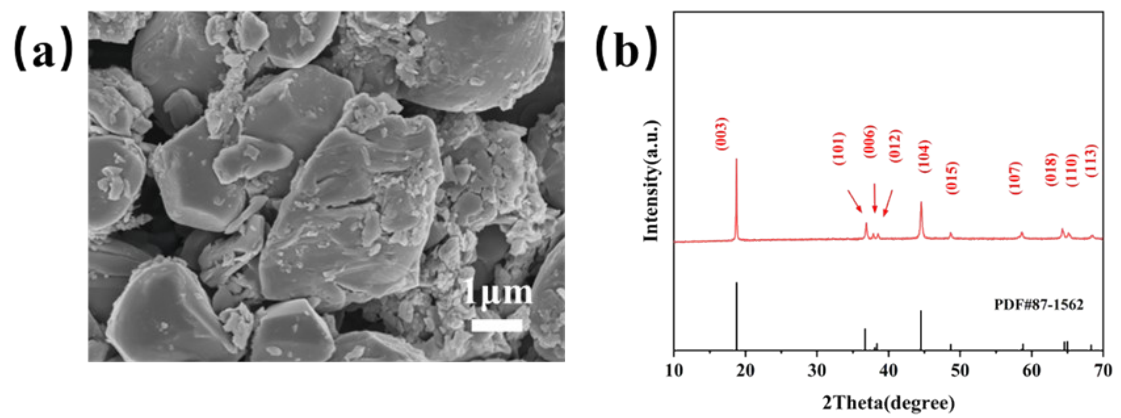
Fig. S6. (a) SEM image and (b) XRD pattern of the Ni55 cathode material before separation.
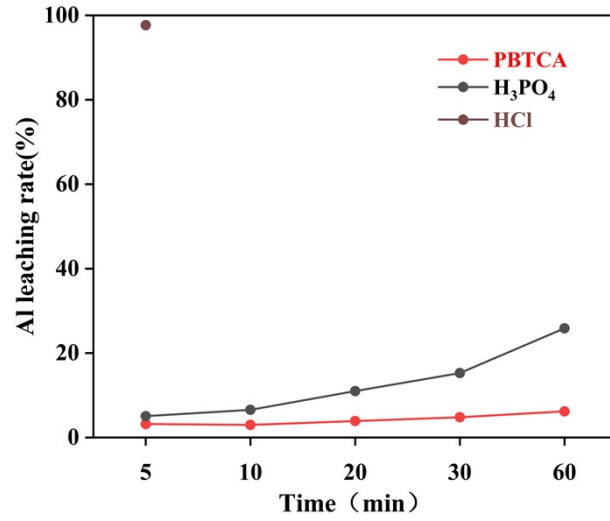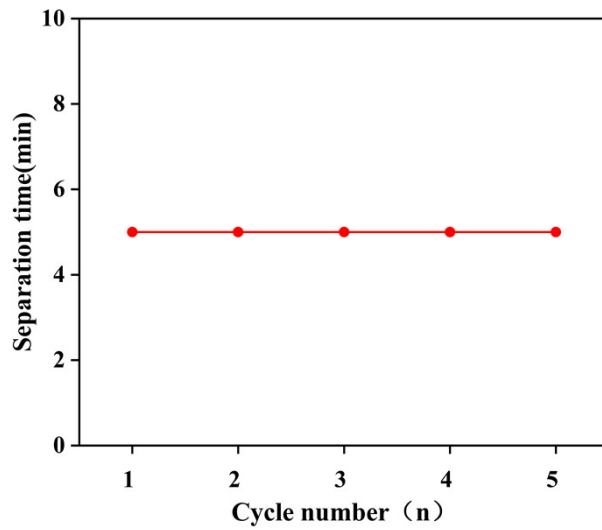
Fig. S7. High-resolution (a) C 1s and (b) O 1s XPS of Al foil that was separated using PBTCA.

Fig. S8. High-resolution Al 2p, O 1s, and P 2p XPS of Al foil separated using (a) EDPA and (b) PPA.

Fig. S9. Time-dependent leaching rate of Al in PBTCA solution.

Fig. S10. The separation time of Ni55 cathode sheets in the repeated use of PBTCA solution versus the cycle number.
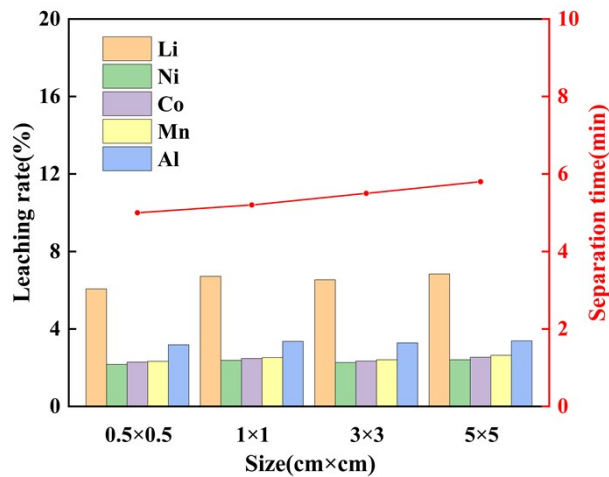
Fig. S11. Effect of Ni55 cathode sheet size on the separation time and the leaching rates of Al, Li, Ni, Co, and Mn.
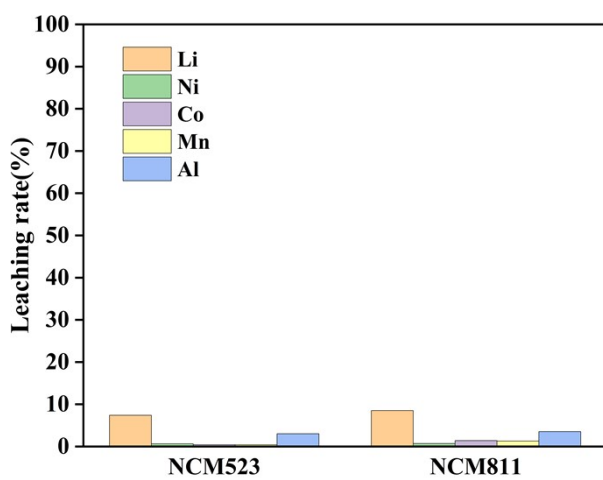
Fig. S12. Li, Ni, Co, Mn, and Al leaching rates from NCM523 and NCM811 in 10wt% PBTCA solution.
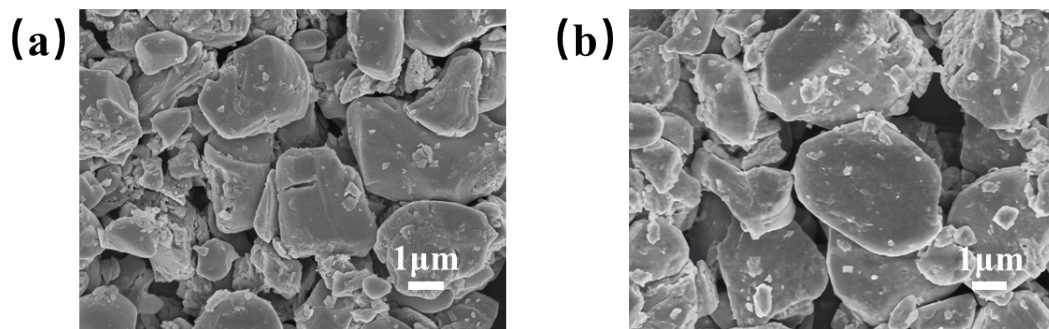
Fig. S13. (a) SEM of separated Ni55 cathode material and (b) regenerated Ni55.
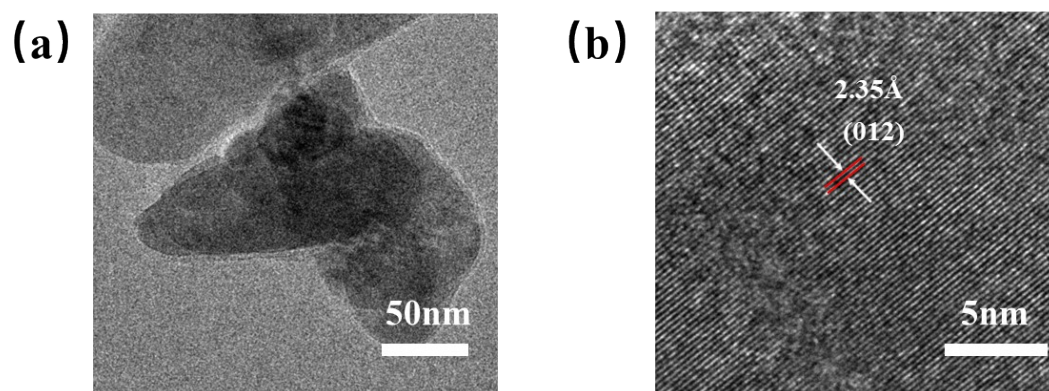
Fig. S14. (a) TEM and (b) HRTEM images of regenerated Ni55.
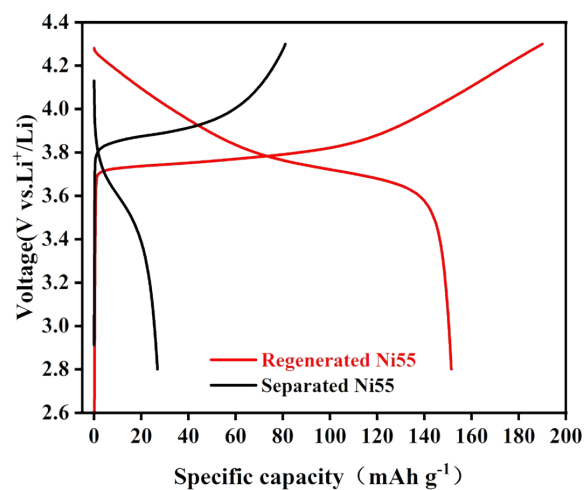
Fig. S15. First charge-discharge curves of Ni55 before and after regeneration at 0.1 C.
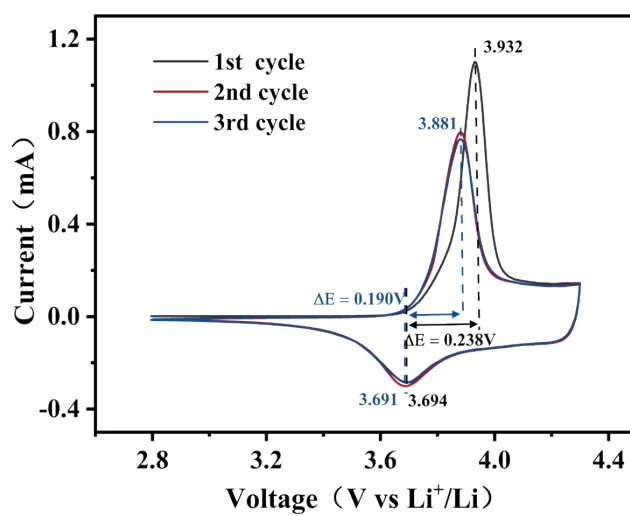
Fig. S16. CV curve of the regenerated Ni55.
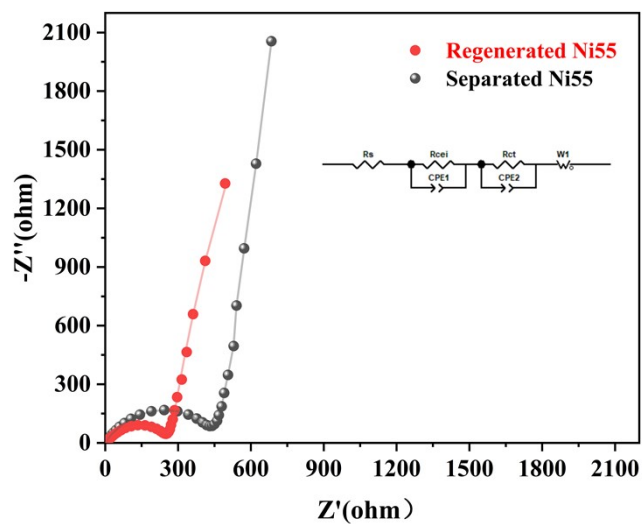
Fig. S17. EIS plots of the separated and regenerated Ni55.
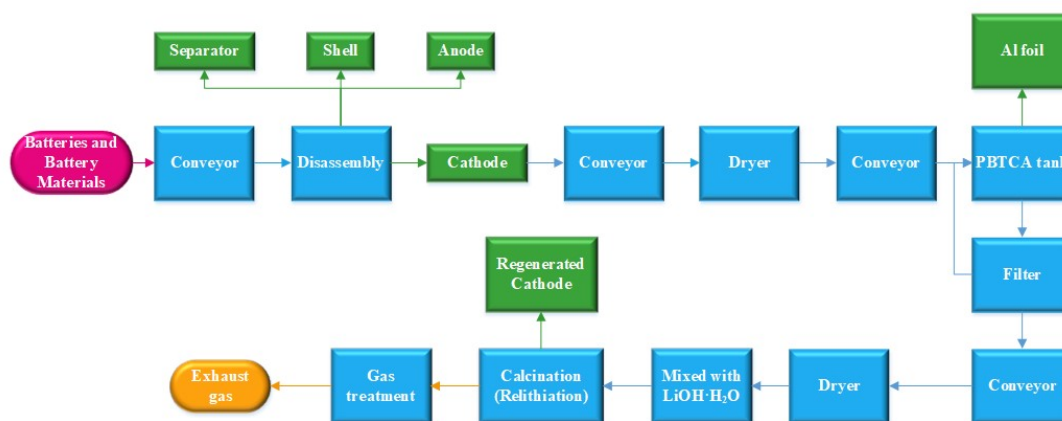
Fig. S18. Diagram of PBTCA-based recycling process.

Fig. S19. Diagram of the direct recycling process developed by the Argonne National Laboratory.
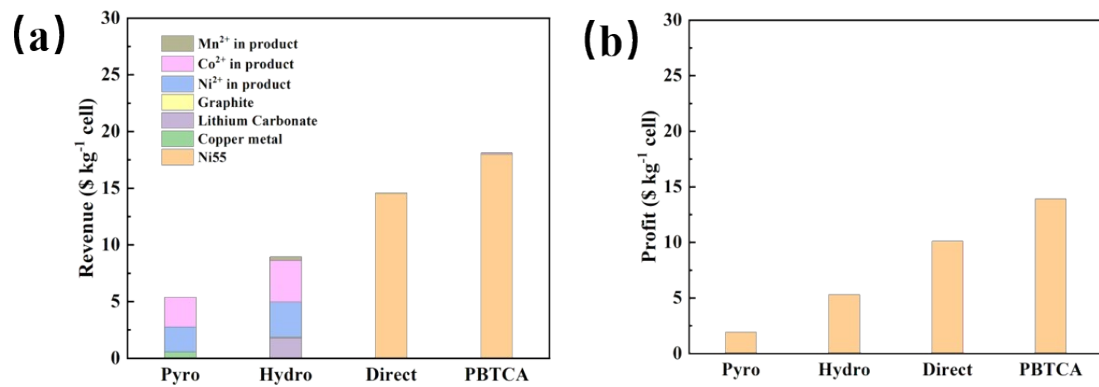
Fig. S20. Economic and environmental analysis of PBTCA and other recycling methods (Hydro, Pyro, and Direct). (a) Revenue. (b) Profit.

Table S1. A price comparison of PBTCA, PPA, and EDPA.

	Price ($ g^{-1})
PBTCA	0.17
PPA	9.53
EDPA	47.04

Table S2. LCA and TEA of different recycling approaches.

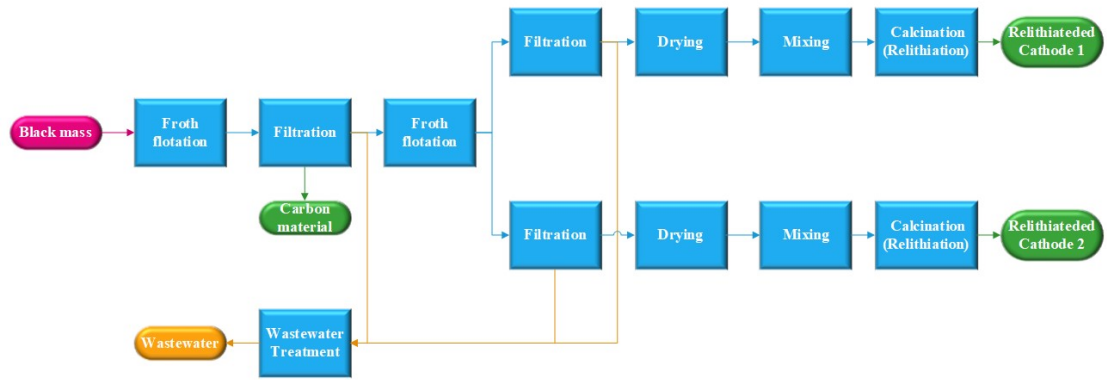|	Pyro	Hydro	Direct	PBTCA
Total energy (MJ kg^{-1}, cell)				
Total Energy	4.45	33.87	30.49	19.02
Fossil fuels	3.91	30.90	26.91	17.89
Coal	2.39	10.32	20.20	9.73
Natural gas	0.64	20.94	6.61	3.71
Petroleum	0.87	4.84	5.30	4.45
Water consumption (liter/kg)	5.70	16.94	14.53	10.40
Total Emissions: grams/kg				
VOC	0.07	0.38	0.35	0.30
CO	0.28	1.58	1.32	1.05
NO$_x$	0.72	2.88	3.04	2.70
PM10	0.07	0.28	0.42	0.35
PM2.5	0.05	0.19	0.26	0.26
SO$_x$	1.17	3.33	2.30	1.97

BC	0.01	0.04	0.04	0.04
OC	0.01	0.05	0.05	0.06
CH_4	0.55	5.10	4.05	2.47
N_2O	0.01	0.05	0.05	0.02
CO_2	1,726	2,358	2,496	1,487
CO_2 (w/ C in VOC & CO)	1,727	2,362	2,499	1,489
GHGs	1,745	2,527	2,633	1,568
Revenue ($ kg^{-1}, cell)	5.40	8.96	14.59	18.11
Cost($ kg^{-1}, cell)	3.47	3.66	4.48	4.19
Profit($ kg^{-1}, cell)	1.93	5.30	10.11	13.92

Table S3. Energy consumption of different recycling approaches (MJ kg^{-1}, cell).

	Material input	Energy input	Total
Pyro	0.82	3.63	4.45
Hydro	32.24	1.63	33.87
Direct	11.22	19.27	30.49
PBTCA	17.48	1.54	19.02

Table S4. GHG emission of different recycling approaches (g kg^{-1}, cell).

	Material input	Energy input	Process
Pyro	0.13	0.28	1.34
Hydro	2.40	0.13	-
Direct	1.05	1.58	-
PBTCA	1.45	0.12	-

Table S5. Water consumption of different recycling approaches (L kg^{-1}, cell).

	Material input	Energy input	Process
Pyro	0.57	1.36	3.79
Hydro	14.42	1.10	1.40
Direct	4.61	6.51	3.41
PBTCA	6.30	0.36	3.78

Table S6. Cost of different recycling approaches ($ kg^{-1}, cell).

	Pyro	Hydro	Direct	PBTCA
Materials	1.68	2.16	2.73	3.73
Utilities	0.03	0.06	0.20	0.01
Other variable costs	0.04	0.05	0.06	0.07
Labor	0.03	0.07	0.07	0.05
Maintenance	0.18	0.13	0.14	-
Plant overhead	0.11	0.18	0.23	0.26
Other fixed costs	0.26	0.20	0.22	0.07
Annualized capital cost	1.13	0.80	0.83	-

Table S7. Revenue of different recycling approaches ($ kg^{-1}, cell).

	Pyro	Hydro	Direct	PBTCA
Copper metal	0.56	-	-	-
Graphite	-	0.07	-	-
Lithium Carbonate	-	1.80	-	-
Aluminum	-	-	-	0.11
Ni^{2+} in product	2.20	3.08	-	-
Co^{2+} in product	2.64	3.69	-	-
Mn^{2+} in product	-	0.32	-	-
Ni55 product	-	-	14.52	18.00