## **Supporting Information**

## Full Recovery of Lithium Salts and Transition Metal Oxides from Spent Ternary Cathode Lithium-Ion Batteries

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## **Experimental Section**

**Materials and Chemicals:** Tetraethylammonium chloride (TEAC, >98%), oxalic acid dihydrate (OxA,  $\geq$ 99.5%), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, AR, 30 wt. % in H<sub>2</sub>O), potassium hydroxide (KOH, AR), and anhydrous ethanol (AR) were purchased from Aladdin Biochemical Technology Co., Ltd. The cathode materials (LiNi<sub>0.83</sub>Co<sub>0.12</sub>Mn<sub>0.05</sub>O<sub>2</sub>, S-NCM) were sourced from discarded pouch cells in the laboratory, obtained through manual disassembly, and roasted to eliminate electrolytes and binders. Deionized water was used for all experiments.

**Preparation of DES:** DES were synthesized via a simple procedure involving heating and stirring. Specifically, TEAC and OxA were combined in a molar ratio of 1:1 and stirring at 70 °C for 10 minutes in a flask without any further treatment, resulting in a colorless and transparent liquid.

**Metal Leaching Experiments:** S-NCM was mixed with DES at various solid-to-liquid mass ratios ranging from 1:10 to 1:30, while a specified molar ratio of  $H_2O_2$  solution (with  $n_{H2O2}$ :  $n_{S-NCM}$  varying from 0.05 to 0.25) was simultaneously introduced. The resulting mixture was then subjected to magnetic stirring at 500 rpm under different temperature conditions (spanning from 40°C to 80°C) for multiple time intervals (ranging from 15 to 75 minutes). The leaching efficiencies (E) were determined using the following equation:

$$E = \frac{C_x \times V_L}{M \times W_x} \times 100\%$$
<sup>(1)</sup>

where  $C_x$  (g/L) represents the concentration of metal ion "x" in the leachate (with x=Li, Ni, Co, Mn),  $V_L$  denotes the volume of the leachate, M indicates the mass of the raw material, and  $W_x$  reflects the mass percentage of metal x present in the raw material.

**Metal Separation and Recovery:** Upon completion of the leaching process, the resulting leachate was subjected to centrifugation in a high-speed centrifuge at 10,000 rpm for a duration of 5 minutes. The first filter residues were subsequently washed three times with anhydrous ethanol, and the first filtrate was collected separately. Subsequently, 50 milliliters of deionized water were added to the first filtrate and heated to 70°C for 2 h. A significant formation of pink precipitate was observed, which was then separated from the second residue through vacuum filtration. The first and second filter residues were subjected to calcination at 500°C for a duration of 2 h to produce high-purity metal oxides. The second filtrate was evaporated, followed by the addition of 50 mL of

anhydrous ethanol. The resulting mixture was then reacted at a temperature of 60°C for a duration of 2 h. Subsequently, the third filter residues were obtained through filtration. The third filtrate underwent evaporation, after which an appropriate amount of KOH solution was added to adjust the pH to 12, leading to the formation of the fourth filter residues. This fourth filter residues were subsequently calcined at 500°C for 3 h to yield high-purity manganese dioxide. Upon the completion of the entire process, the recovered products will be dissolved to evaluate their purity and yield. The purity (P) was defined as:

$$P = \frac{w_x}{w_{Li} + w_{Ni} + w_{Co} + w_{Mn}} \times 100\%$$
(2)

The recovery yield  $(\eta)$  was defined as:

$$\eta = \frac{m_x \times g_x}{M \times W_x} \times 100\% \tag{3}$$

where  $w_x$  represents the final mass fraction of element x (Li, Ni, Co, or Mn) in the solution (ppm), while  $w_{Li}$ ,  $w_{Ni}$ ,  $w_{Co}$ , and  $w_{Mn}$  denote the final mass fractions of Li, Ni, Co, and Mn, respectively.  $m_x$ represents the mass of the ultimate recovered products of metal element x (Li, Ni, Co, or Mn),  $g_x$ indicates the mass fraction of element x in the recovered products.

**Resynthesis of the Cathode Material:** The recovered  $Li_2C_2O_4$  and  $Co_3O_4$  were combined in a specific stoichiometric ratio, incorporating a 5% excess of Li. Subsequently, the mixture will undergo ball milling at 300 rpm for 6 h. Following this process, it will be subjected to calcination in a muffle furnace at 1000°C for 10 h, after which the calcination will continue at 900°C for an additional 10 h. This procedure is expected to yield the resynthesized LiCoO<sub>2</sub> (R-LCO). Similarly, the recovered  $Li_2C_2O_4$  and MnO<sub>2</sub> were sintered at 800°C for 12 h, resulting in the resynthesized  $LiMn_2O_4$  (R-LMO). Finally, the recovered  $Li_2C_2O_4$ , NiO,  $Co_3O_4$ , and MnO<sub>2</sub> were mixed in a specific stoichiometric ratio, pre-sintered at 500°C for 6 h, and then calcined at 900°C for 12 h, resulting in the resynthesized  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  (R-NCM523).

Battery Assembly and Testing: The samples (R-LCO, R-LMO, and R-NCM523) were mixed with polyvinylidene fluoride (PVDF) and carbon black in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 8:1:1. Subsequently, the resulting slurries were coated onto aluminum foil and dried under vacuum at 120 °C for 12 h. Coin cells (2032) were assembled using a lithium metal disc (thickness 450  $\mu$ m) as the anode, with an electrolyte composed of 1 M LiPF<sub>6</sub> in ethylene carbonate (EC):ethyl methyl carbonate (EMC) at a weight ratio of 3:7, supplemented with 2% vinylene carbonate (VC). A Celgard 2400 membrane was employed as the separator.

Galvanostatic charge-discharge measurements and cycling performance were conducted using LAND and Neware battery testing systems within the potential ranges of 2.8-4.3 V (for R-NCM523) or 3.0-4.3 V (for R-LCO and R-LMO) relative to Li/Li<sup>+</sup>. The first cycle was initiated with an activation current of 0.2 C. The cycling performance was evaluated at a rate of 0.5 C within the same voltage range.

Materials Characterization: Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Avio 200) was utilized to quantify the concentration of metal ions present in the solution. The X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance instrument with Cu K<sub>a</sub> ( $\lambda = 1.5418$  Å), covering a range from 10° to 80°. The Fourier transform infrared (FTIR) spectra were executed by FTIR spectroscope (PerkinElmer, Spectrum Two LiTa) with a wavenumber range of 4000–400 cm<sup>-1</sup>. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained on a BRUKER AVANCEIIIHD 500 Nuclear Magnetic Resonance spectrometer. Thermogravimetric analysis was performed using a TA Instruments SDT Q600 in an O<sub>2</sub> atmosphere, spanning from room temperature to 330°C. The Scanning Electron Microscope (SEM; Hitachi Regulus 8100) was utilized to characterize the morphology of the materials. Ultraviolet–visible (UV-vis) absorption spectra were recorded using a UV-visible spectrophotometer (Shimadzu, UV-3600 Plus).



**Fig. S1** Preparation of the DES. (a) The preparation of DES employing TEAC and OxA. (b) Schematic illustration of the hydrogen bonding interactions between TEAC and OxA.



Fig. S2 The alterations in the solution before and after the leaching process.



**Fig. S3** A comparative analysis of the leaching capabilities of a 1 M oxalic acid solution and DES. The results indicate that under these same conditions, oxalic acid is only able to extract a limited fraction of Li from S-NCM, while it proves nearly ineffective in extracting Ni, Co, and Mn. These findings illustrate that DES significantly outperforms oxalic acid solution alone in terms of leaching efficacy and demonstrates superior selectivity for the extraction and separation of metals.



Fig. S4 FTIR spectra of the first filter residues. The spectrum of the precipitate exhibits an O-H stretching vibration peak at 3392 cm<sup>-1</sup>, an asymmetric stretching vibration at 1621 cm<sup>-1</sup>, and symmetric stretching vibrations at 1361 cm<sup>-1</sup> and 1317 cm<sup>-1</sup>, all of which align with the characteristics of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.



**Fig. S5** Battery recycling schematic. The process begins with the disassembly of LIBs, after which the cathode waste is introduced into the DES. This mixture is then subjected to heating and stirring, facilitating the selective precipitation of Ni while effectively leaching Li, Co, and Mn. Valuable metal elements are subsequently recovered in the form of precipitates for future reutilization.



Fig. S6 The intermediates that were recovered, listed from left to right, include  $NiC_2O_4 \cdot 2H_2O$ ,  $CoC_2O_4 \cdot 2H_2O$ ,  $Li_2C_2O_4$ , and manganese precipitate.



Fig. S7 XRD patterns of (a) R-LCO, (b) R-LMO, and (c) R-NCM523.



Fig. S8 SEM images of R-LCO, accompanied by EDS analysis.



Fig. S9 SEM images of R-LMO, accompanied by EDS analysis.



Fig. S10 SEM images of R-NCM523, accompanied by EDS analysis.



**Fig. S11** Electrochemical performance of cathodes synthesized using commercial materials. (a) Charge and discharge curves of C-LCO at 0.2 C and 1 C Rates. (b) Cycling performance of C-LCO at 1C Rate. (c) Charge and discharge curves of C-LMO at 0.2 C and 1 C Rates. (d) Cycling performance of C-LMO at 1C Rate. (e) Charge and discharge curves of C-NCM523 at 0.2 C and 1 C Rates. (f) Cycling performance of C-NCM523 at 1C Rate.



Fig. S12 The leaching efficiency of various cathode materials employing DES.



**Fig. S13** (a) Raman spectra of Ni precipitation (b) Raman spectra of Co precipitation (c) Raman spectra of the solution before and after leaching reaction.

 Table S1 The initial elemental composition of the recovered ternary cathode materials in this experiment.

Elements	Li	Ni	Co	Mn
Concentration	0.176 mg/L	1.219 mg/L	0.182 mg/L	0.064 mg/L
Molar ratio	1	0.83	0.12	0.05

Temperature	Lithium concentration	Nickel concentration	Cobalt concentration	Manganese concentration
40°C	0.352 mg/L	0.050 mg/L	0.190 mg/L	0.041 mg/L
50°C	0.401 mg/L	0.054 mg/L	0.323 mg/L	0.104 mg/L
60°C	0.710 mg/L	0.061 mg/L	0.712 mg/L	0.244 mg/L
70°C	0.779 mg/L	0.064 mg/L	0.800 mg/L	0.280 mg/L
80°C	0.778 mg/L	0.072 mg/L	0.802 mg/L	0.279 mg/L

 Table S2 The concentration of metallic elements in the leachate following leaching at various temperatures.

Time	Lithium	Nickel	Cobalt	Manganese
Time	concentration	concentration	concentration	concentration
15 min	0.313 mg/L	0.013 mg/L	0.220 mg/L	0.060 mg/L
30 min	0.624 mg/L	0.026 mg/L	0.599 mg/L	0.204 mg/L
45 min	0.735 mg/L	0.054 mg/L	0.728 mg/L	0.252 mg/L
60 min	0.779 mg/L	0.064 mg/L	0.800 mg/L	0.280 mg/L
75 min	0.779 mg/L	0.071 mg/L	0.801 mg/L	0.281 mg/L

 Table S3 The concentration of metallic elements in the filtrate following leaching for various durations.

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solid-to-liquid	Lithium	Nickel	Cobalt	Manganese
mass ratio	concentration	concentration	concentration	concentration
1/10	0.482 mg/L	0.058 mg/L	0.462 mg/L	0.160 mg/L
1/15	0.627 mg/L	0.061 mg/L	0.598 mg/L	0.209 mg/L
1/20	0.713 mg/L	0.062 mg/L	0.732 mg/L	0.254 mg/L
1/25	0.779 mg/L	0.064 mg/L	0.800 mg/L	0.280 mg/L
1/30	0.777 mg/L	0.066 mg/L	0.799 mg/L	0.279 mg/L

**Table S4** The concentration of metallic elements in the filtrate following leaching at various solid-to-liquid mass ratios.

$n_{\rm H2O2}/n_{\rm S-NCM}$	Lithium	Nickel	Cobalt	Manganese
	concentration	concentration	concentration	concentration
0.05	0.456 mg/L	0.047 mg/L	0.411 mg/L	0.124 mg/L
0.10	0.545 mg/L	0.057 mg/L	0.536 mg/L	0.186 mg/L
0.15	0.746 mg/L	0.068 mg/L	0.756 mg/L	0.262 mg/L
0.20	0.779 mg/L	0.064 mg/L	0.800 mg/L	0.280 mg/L
0.25	0.780 mg/L	0.070 mg/L	0.805 mg/L	0.279 mg/L

**Table S5** The concentration of metallic elements in the filtrate following leaching with various amounts of hydrogen peroxide.

Recovered		Elemental concentration / mg L <sup>-1</sup>					
product	Li	Ni	Co	Mn	K	Purity/ %	
NiO	0.000	2.347	0.015	0.005	0.000	99.13	
Co <sub>3</sub> O <sub>4</sub>	0.000	0.007	1.928	0.016	0.000	98.71	
$Li_2C_2O_4$	0.531	0.000	0.064	0.031	0.000	97.88	
MnO <sub>2</sub>	0.000	0.000	0.008	2.116	0.014	98.69	

**Table S6** The purity of the recovered products.

Re-synthesized		Elemental comp	position / mg L <sup>-1</sup>	
cathode	Li	Ni	Со	Mn
R-LCO	0.211	0.000	1.739	0.000
R-LMO	0.086	0.000	0.000	1.274
R-NCM523	0.374	1.548	0.627	0.855

 Table S7 Elemental composition of the resynthesized cathodes.