Electronic supplementary information

Ethylene glycol-inorganic solvents for the sustainable recycling of lithium-ion battery cathodes

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Note S1. Characterization Methods

DSC analysis

The melting points or glass transition temperatures were tested by differential scanning calorimetry (Q200, TA Instruments Company, America) with a heating rate of 10 ºC·min^{-1}. The temperature range tested was from -100 ºC to the room temperature.

FTIR, NMR and UV-vis spectra

Fourier transform infrared (FT-IR) spectra were recorded on an FT-IR spectrometer (Thermo iS50, Thermo Fisher Scientific Inc., Germany) in the range of 400 to 4000 cm^{-1}. ^{1}H-NMR spectra were analyzed by an NMR spectrometer (Bruker Avance III 500, Bruker Corporation, America) after the samples were dissolved in dimethyl sulfoxide-d6. The Ultraviolet-visible (UV-vis) spectra of metal loaded DESs and the absorbance of Hammett acidity measurement were recorded using an UV-Vis-NIR spectrophotometer (UH5300, Hitchi High-Tech Corporation, Japan).

Viscosity, Hammett acidity and cyclic voltammetry

The viscosity was tested on a rotational rheometer (HAAKE RheoSterss 6000, Thermo Fisher Scientific, Germany) from 30 to 90 ºC at a shearing rate of 10 s^{-1}.

EG-inorganic salts solvents, anhydrous ethanol (as all-alkali type solution), and 98% H_2SO_4 (as all-proton type solution) were separately added in 25 mL volumetric flasks with an indicator (4-nitroaniline, $pK_{BH^+} = 0.99$, peak wavelength at 377.5 nm[1]) concentration of 8.5 mg·L^{-1}. Then, the mixed solutions were configured to measure the

Hammett acidity by UV-Vis. The solvents to be tested were prepared by twice dilutions for the accuracy. The Hammett acidity is defined by equation: $H_0 = pK_{BH^+} - lg\,(\frac{C_{BH^+}}{C_B})$, where K_{BH^+} is ion equilibrium constant of 4-nitroaniline, and $\frac{C_{BH^+}}{C_B}$ is proton type concentration of the indicator to the base type concentration of the indicator. According to Lambert-Beer law, $\frac{C_{BH^+}}{C_B}$ at a fixed wavelength is: $\frac{C_{BH^+}}{C_B} = \frac{A_B^{\lambda} - A^{\lambda}}{A^{\lambda} - A_{BH^+}^{\lambda}}$, where A_B^{λ} , $A_{BH^+}^{\lambda}$, A^{λ} are the absorptions at the wavelength of 377.5 nm of anhydrous ethanol, 98% H_2SO_4, and tested solvents with 4-nitroaniline concentration of 8.5 mg·L^{-1}, separately. The measuring operations were maintained at a constant temperature of 25 ºC.

Pt, Pt, and Ag were immersed in DES 5 mm, 10 mm, and 5 mm as the work electrode, counter electrode, and reference electrode to obtain cyclic voltammetry, which was operated by electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd, China) as a function of temperature at 50 ºC and 90 ºC in different EG-inorganic salts solvents. The scan rate was 50 mV·s^{-1} and the data of the fifth test cycle was selected as the results. Before the test, the electrodes were cleaned with absolute ethanol and deionized water, and the temperature of DES was maintained for 20 min. The open circuit potential measurement time was 180 s.

ICP-OES analysis and dissolution ratio calculation

The concentration of metals was analyzed by an inductively coupled plasma optical atomic emission spectrometry (ICP-OES,730-ES, Varian Inc., America). The former data was used to calculate dissolution ratio by equation: $D = \frac{w_{M,d} \cdot m_{DES}}{m_{M,r}} \cdot 100\%$, where

$w_{M,d}$ means the mass concentration of metal in DES with the unit of g·g^{-1}, the m_{DES} means the mass of DES after dissolution, and the $m_{M,r}$ is the original mass of metal before dissolution.

XRD analysis

The structures of powder produced in experiments were measured with a Rigaku 114 Ultima IV diffractometer (Rigaku Corporation, Japan) using Cu Kα radiation (λ=1.54184 Å) at a scanning rate of 2 °·min^{-1}.

GC-MS analysis

The syringe was sampled with 0.2 μL and the separation ratio was 5:1. The temperature of the inlet was set at 270 °C under programmed, and the exit temperature of the chromatographic column was 40 °C. The heating rate was 10 °C·min^{-1}. When the temperature reached the set temperature of the inlet, it was maintained for 5 min. The MS transmission line temperature was set at 270 °C, and the MS solvent was no delay. The detector was turned off for 3-3.2 min, with the scanning mass-charge ratio of 29-550.

Note S2. Technoeconomic analysis of the recovery process

In the recovery process of spent LCO with 3 cycles, the total chemicals consumption contained 44.4 g EG, 5.6 g $AlCl_3·6H_2O$, 2.75 g $H_2C_2O_4$ and 2.78 g NaOH. The total products of recovered process were 2.3 g Co_3O_4, 0.83 g Al_2O_3 and a LiCl solution containing 0.8 g of LiCl. The total energy consumption contains the electricity utilization during leaching and calcination. A power converter was used to calculate the power of each process.

(1) Material costs. The prices of all the raw chemicals and regents were based on the prices on varied regent companies. The total prices were calculated as: 8 $ kg^{-1} × 44.4/1000 kg ($0.35, EG) +11.4 $ kg^{-1} ×5.6/1000 ($ 0.064, $AlCl_3 \cdot 6H_2O$) +20 $ kg^{-1} ×2.75/1000 ($ 0.055, $H_2C_2O_4$) + 0.7 $ kg^{-1} × 2.78/1000 kg ($0.002, NaOH) =$0.47.

(2) Energy consumption costs. The price of electricity in Zhejiang, China is $ 0.0729 per kWh. The total prices were calculated as $ 0.0729/kWh × 0.4 kW × 9 h (leaching) + $ 0.0729/kWh × 3.247 kW × 12 h (calcination) = $3.1. So, the cost of materials and electricity were $0.47+$3.1=$3.57.

The prices of all obtained products were calculated as: 4714 $ kg^{-1} × 2.3/1000 kg ($10.84, Co_3O_4) +14.29 $ kg^{-1} ×0.83/1000 ($ 0.012, Al_2O_3) +199.9 $ kg^{-1} ×0.8/1000 ($ 0.16, LiCl) = $11.01.

Supplementary Figures

Figure S1. Images of several EISs.

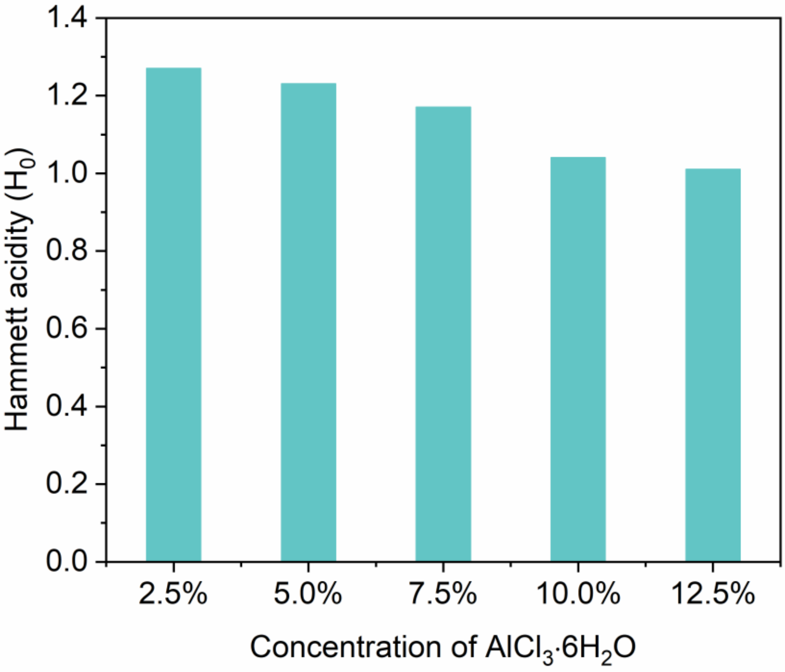


Figure S2. Hammett acidity of aqueous $AlCl_3 \cdot 6H_2O$ solutions.

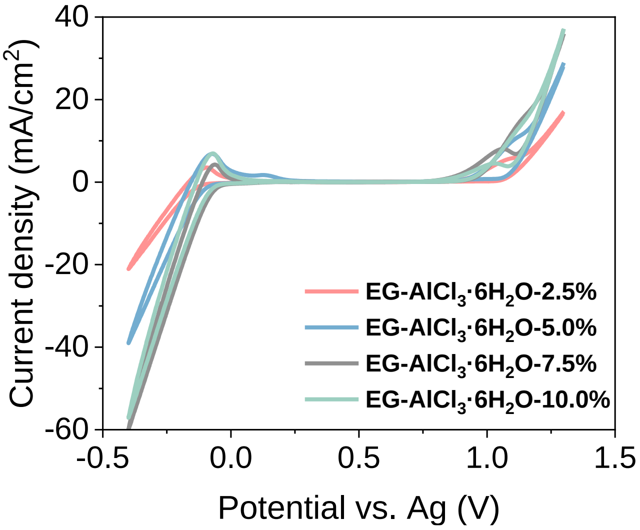


Figure S3. Cyclic voltammogram curves of EISs without $AlCl_3 \cdot 6H_2O$ at 50 ℃. There was no reducing peak in these curves of EISs.

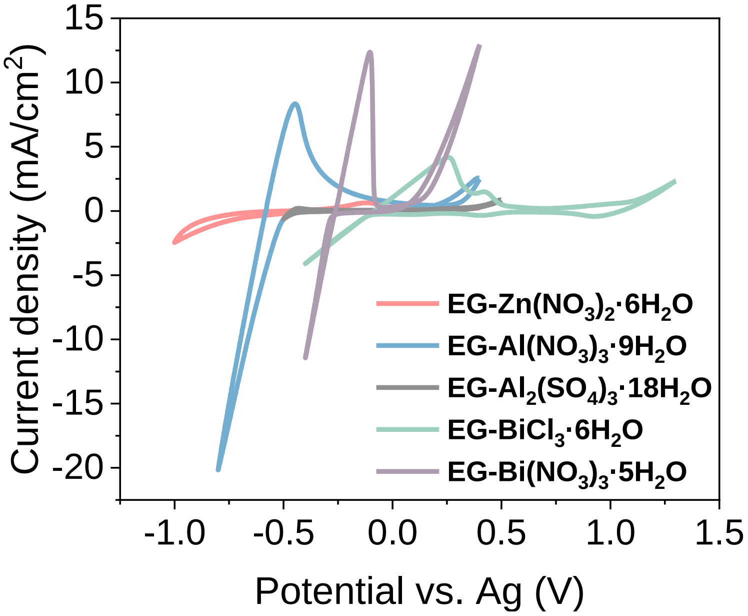


Figure S4. Cyclic voltammogram curves of other EISs with different $AlCl_3·6H_2O$ content at 50 ℃. There was no reducing peak in these curves of EISs.

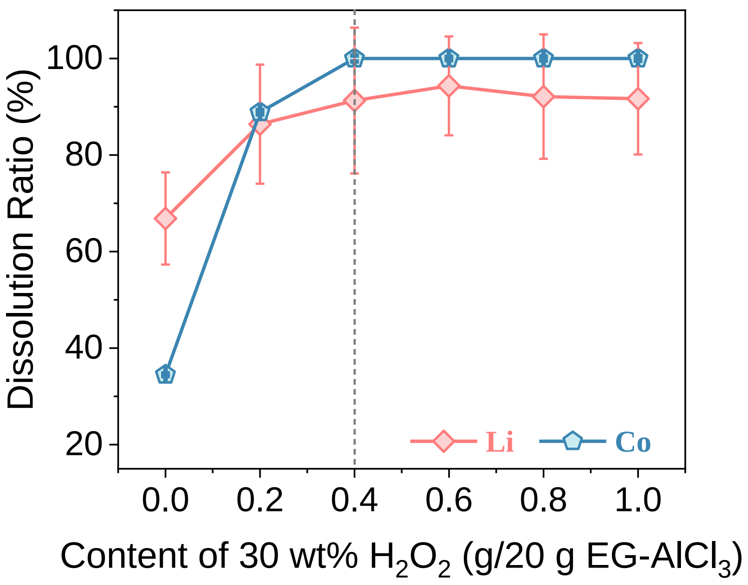


Figure S5. The effect of H_2O_2 content on the dissolution ratio of LCO.

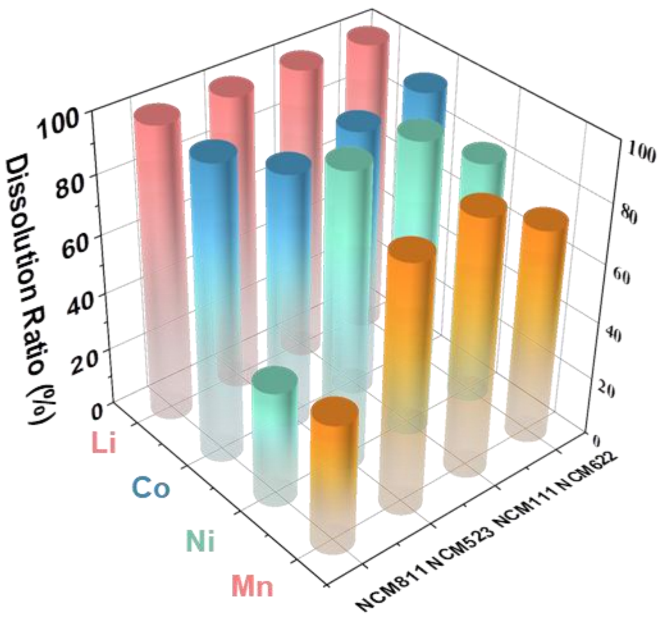


Figure S6. Dissolution ratios of Li, Co, Ni, and Mn in four kinds of NCMs in EG-$AlCl_3 \cdot 6H_2O$ at 90 °C.

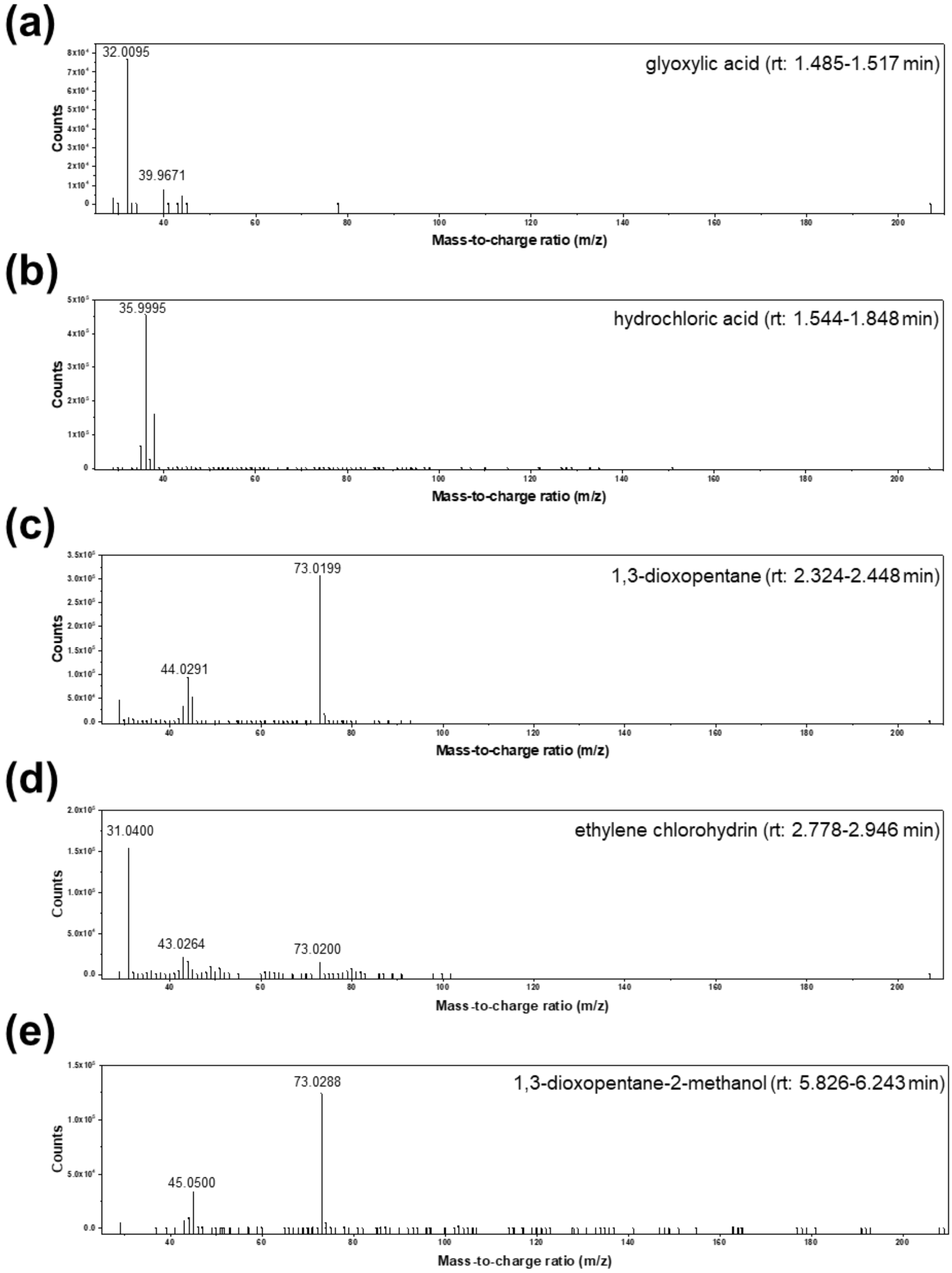


Figure S7. MS spectrum of leachate at 90 ºC, the matter peak appearing (a) in 1.501 min, (b) 1.626 min, (c) 2.368 min, (d) 2.843 min, (e) 6.129 min.

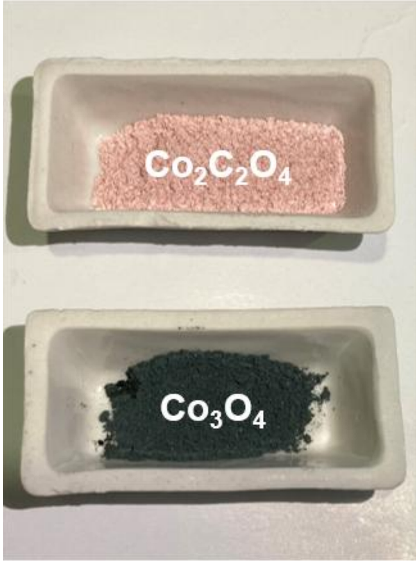


Figure S8. Images of recovered $Co_2C_2O_4$ and Co_3O_4.

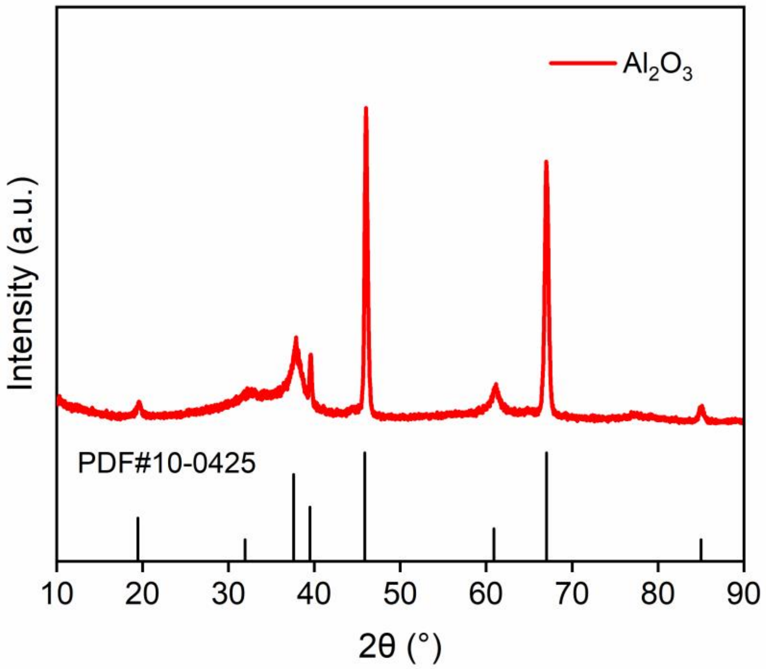


Figure S9. XRD patterns of recovered Al$_2$O$_3$.

Supplementary Tables

Table S1. The solubility of inorganic salts in EG, and the dissolution ratios of LCO in EISs. (The default dissolution conditions were T = 50 ℃, t = 6 h, solid: liquid = 1:50, mole ratio of EG-inorganic salt = 0.645:0.0206 and stirring rate = 400 rpm, unless the condition varied)

EIS	Solubility	Dissolution Ratio of Li (%)	Dissolution Ratio of Co (%)
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/5 g	Yes	66.43	42.97
EG-$Al(NO_3)_3 \cdot 9H_2O$	Yes	14.04	7.11
EG-$Al_2(SO_4)_3 \cdot 18H_2O$	Yes	3.54	2.08
EG-$Bi(NO_3)_3 \cdot 5H_2O$	Yes	12.77	10.06
EG-$BiCl_3$	Turbid after dwell	40.45	18.47
EG-$Fe(NO_3)_3 \cdot 9H_2O$	Yes	19.44	17.28
EG-$Cu(NO_3)_2 \cdot 3H_2O$	Yes	1.08	0.22
EG-$Zn(NO_3)_2 \cdot 6H_2O$	Yes	0.47	0.06
EG-$MgCl_2 \cdot 6H_2O$	Yes	1.03	0.06
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/1 g	Yes	22.80	22.83
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/2 g	Yes	40.82	29.75
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/3 g	Yes	47.25	32.76
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/4 g	Yes	51.51	36.95
EG/anhydrous $AlCl_3$ =40 g/0.55 g	Yes	19.77	27.17
EG/anhydrous $AlCl_3$ =40 g/1.10 g	No	-	-
EG/anhydrous $AlCl_3$ =40 g/1.65 g	No	-	-
EG/anhydrous $AlCl_3$ =40 g/2.20 g	No	-	-
EG/anhydrous $AlCl_3$ =40 g/2.75 g	No	-	-

Table S2. The Hammett acidity of several EISs.

EIS	Ionic conductivity(μS/cm)
EG/anhydrous $AlCl_3$ =40 g/0.55 g	1156
EG/$AlCl_3 \cdot 6H_2O$ = 40 g/1 g	1032

Table S3. The Hammett acidity of several EISs.

EIS	Absorbance	Hammett acidity (H_0)
EG-$AlCl_3 \cdot 6H_2O$-H_2O_2	0.868472	2.293692
EG-$Al(NO_3)_3$	0.569330	1.192828
EG-$Al_2(SO_4)_3$	0.908339	3.627425

Table S4. The dissolution ratios of LCO in aqueous $AlCl_3 \cdot 6H_2O$ solutions. (T = 90 ºC, t = 3 h, solid: liquid = 1:50, and stirring rate = 400 rpm)

EIS	Dissolution Ratio of Li (%)	Dissolution Ratio of Co (%)
$EG/AlCl_3 \cdot 6H_2O$ = 40 g/1 g	0	0
$EG/AlCl_3 \cdot 6H_2O$ = 40 g/2 g	0	0
$EG/AlCl_3 \cdot 6H_2O$ = 40 g/3 g	0	0
$EG/AlCl_3 \cdot 6H_2O$ = 40 g/4 g	0	0
$EG/AlCl_3 \cdot 6H_2O$ = 40 g/5 g	0	0

Table S5. The residence time and area ratio of major GC-MS peaks, and their corresponding substances and structural formulas.

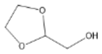
Residence time/min	Area ratio %	Substance	Structural formula
1.501	0.10	glyoxylic acid	$HOOCCH_2CHO$
1.626	20.11	hydrochloric acid	HCl
2.368	7.78	1,3-dioxopentane	
2.843	6.15	ethylene chlorohydrin	$HOCH_2CH_2Cl$
6.129	22.07	1,3-dioxopentane-2-methanol	

Table S6. Summary of LCO recycling using different systems for metals recovery.

	Agents	**Dissolution ratios**	**Recyclable**	**Temperature**	**Reference**
Solvometallurgy	GUC-LAC	97.42% Li, 96.91% Co in 24 h	No	50 °C	2
	EG-MA	98.4% Li, 98.3% Co in 10 h	No	150 °C	3
	EG-ChCl	94% Li, 90% Co in 24 h	Yes	220 °C	4
	EG-$AlCl_3 \cdot 6H_2O$	100% Li, 100% Co in 3 h	Yes	90 °C	This work
	ChCl-urea	61.1% Li, 64.2% Co in 12 h	No	160 °C	5
Hydrometallurgy	1M HNO_3+1.7 vol% H_2O_2	95% Li, 95% Co in 1h	No	75 °C	6
	1M H_2SO_4+ 10 g/L glucose	92% Li, 88% Co in 4h	No	80 °C	7
Pyrometallurgy	$(NH_4)_2SO_4$	91.3% Li, 93.5% Co in 5 h	No	400 °C	8

Table S7. Summary of parameters for LCO recycling using different systems.

	Agents	Agents recycle	Leaching efficiency	Environmental friendliness	Energy saving
Solvometallurgy	GUC-LAC	0	97.165	80	70
	EG-MA	0	98.35	70	60
	EG-ChCl	100	92	60	30
	EG-$AlCl_3 \cdot 6H_2O$	100	100	90	90
	ChCl-urea	0	62.65	50	50
Hydrometallurgy	1M HNO_3+1.7 vol% H_2O_2	0	95	40	100
	1M H_2SO_4+ 10 g/L glucose	0	90	30	80
Pyrometallurgy	$(NH_4)_2SO_4$	0	92.4	100	40

*The recyclability of the agents was estimated based on whether the agents are recyclable. The leaching efficiency was estimated based on the average dissolution ratios of Li and Co. Environmental friendliness was an indicator that evaluates the degree of environmental damage and toxicity of secondary pollution generated during the recycling process. The degree of environmental pollution was as follows: inorganic strong acids > volatile organic solvents > inorganic ions[9]. The energy saving was estimated based on the extraction temperature and time. In these four evaluation parameters, higher scores represent better performance.

Reference

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