Supplementary Information

High Solid-to-Liquid Ratio Leaching of Strategic Metals from Spent Lithium-Ion Batteries: Design of a Green and Sustainable Deep Eutectic Solvent System

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Supporting Information include:

Supporting Figures 1 to 23

Supporting Tables 1 to 11

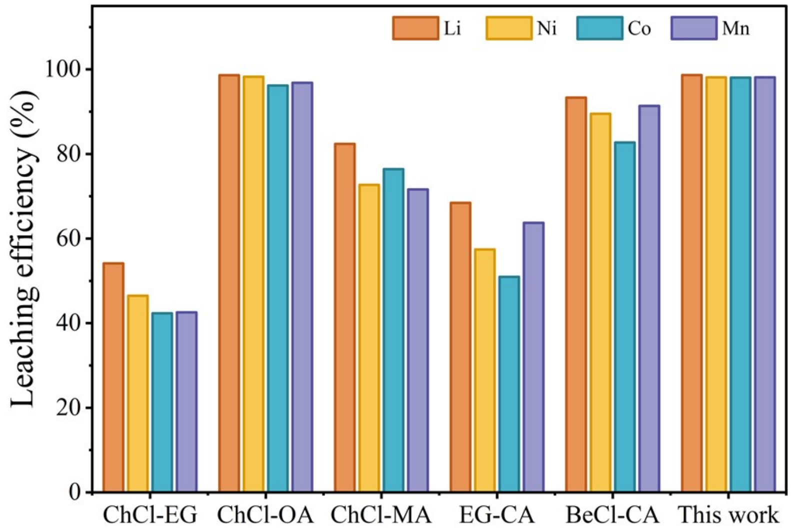


Figure S1 Comparison of leaching efficiencies of different binary DESs.

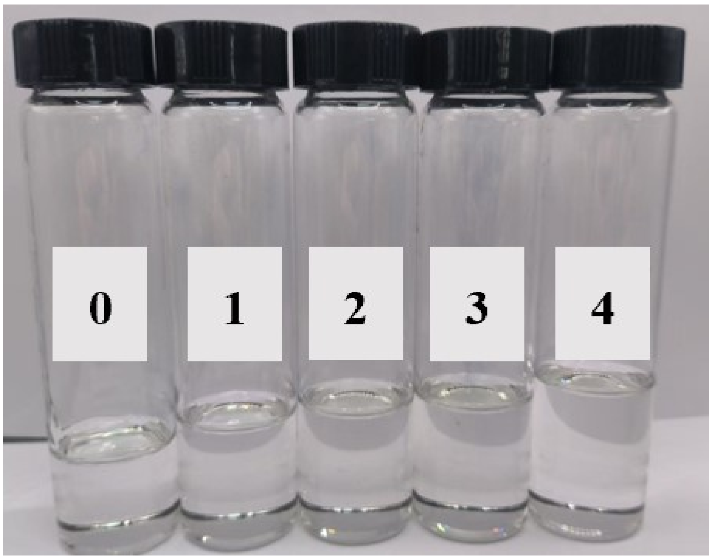


Figure S2 Digital images of DES with varying water content (ChCl:CA:H_2O=1:1:X, X=0-4).

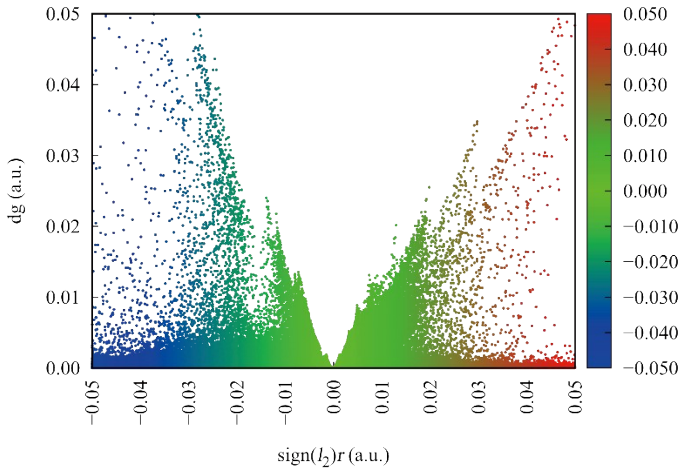


Figure S3 Independent Gradient Model (IGMH) analysis of hydrogen bond formation between choline chloride (ChCl) and citric acid (CA).

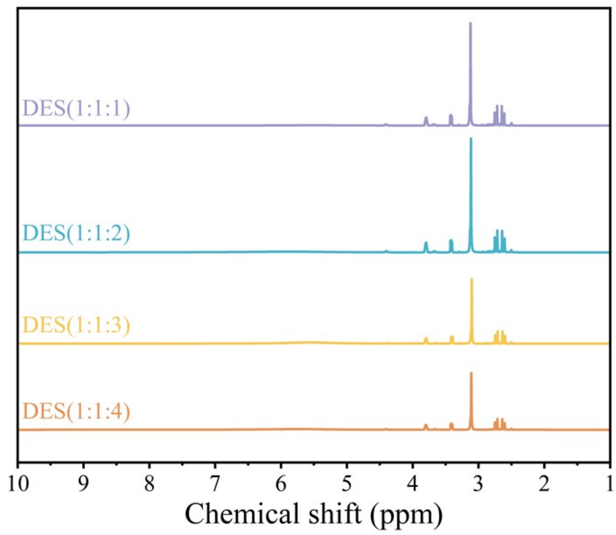


Figure S4 ^{1}H NMR spectra of DES with varying water content (ChCl:CA:H_2O).

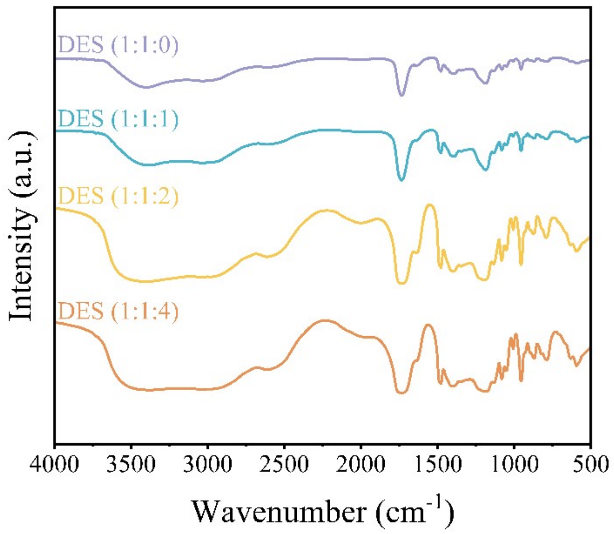


Figure S5 FTIR spectra of DES with varying water content (ChCl:CA:H_2O).

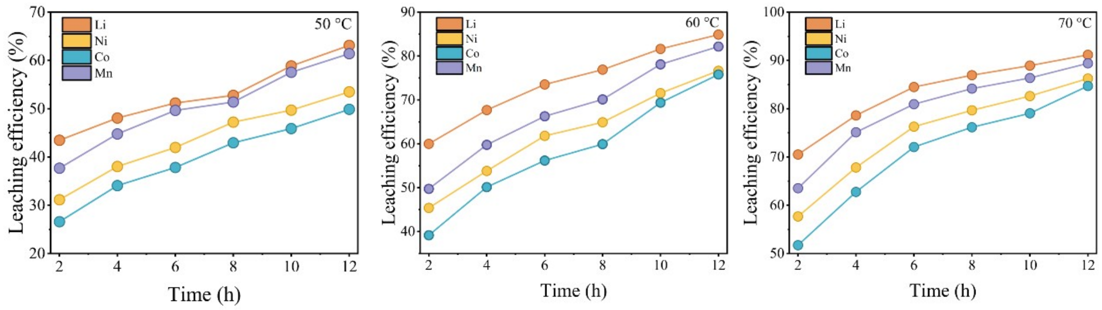


Figure S6 Leaching efficiency trends of Li, Ni, Co, and Mn over time at different temperatures.

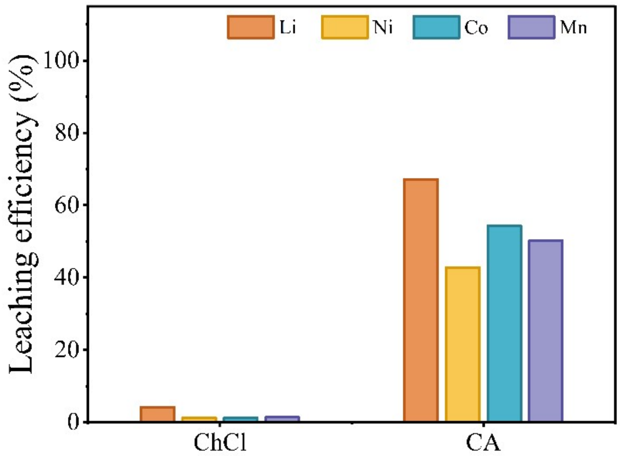


Figure S7 Leaching efficiency of Li, Ni, Co, and Mn in individual ChCl and CA reactions with NCM523 (Temperature=80 °C, leaching time=8 h, slurry concentration (L/S)=15 g/g).

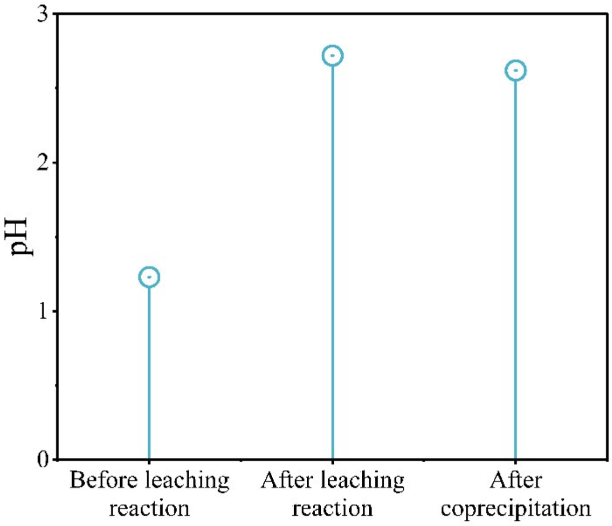


Figure S8 pH variation before and after reaction of DES with NCM523.

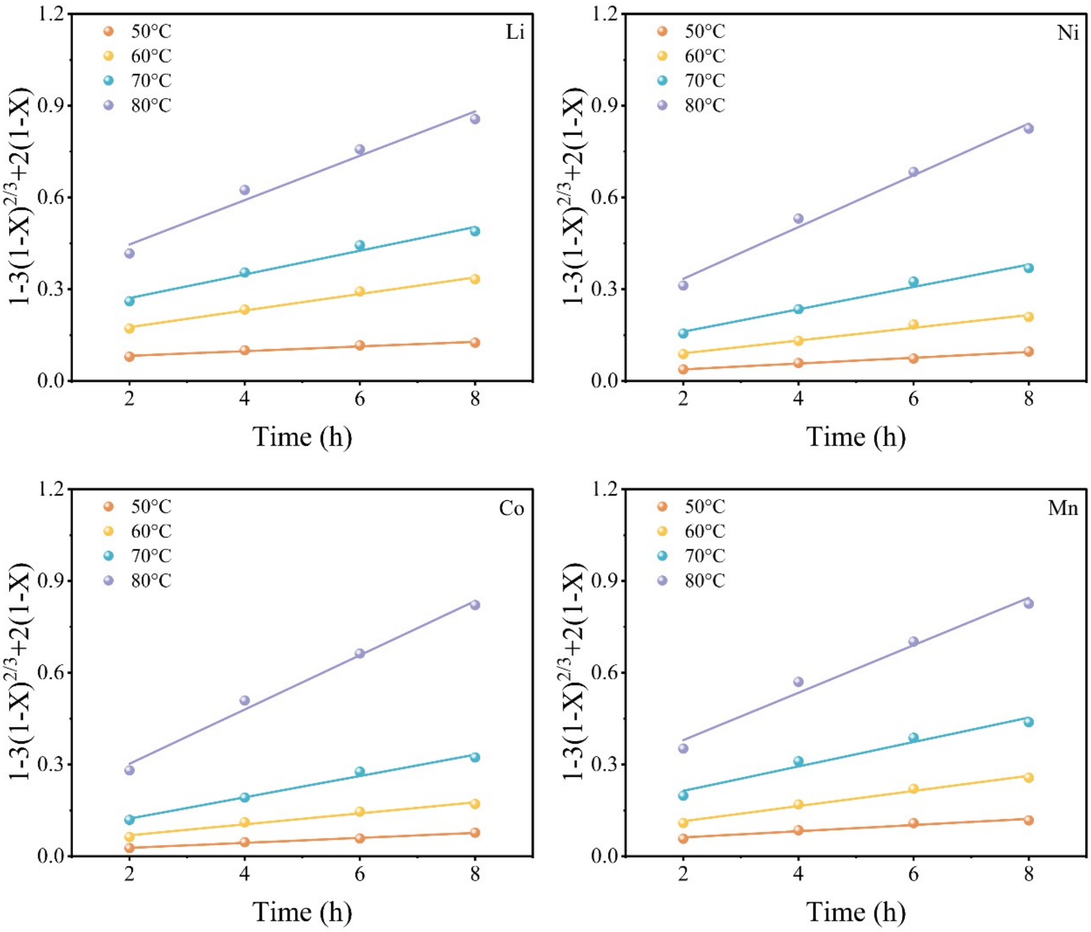


Figure S9 Fitting analysis of $1-3(1-x)^{2/3}+2(1-x)$ for Li, Ni, Co, and Mn in DES leaching system at different temperatures.

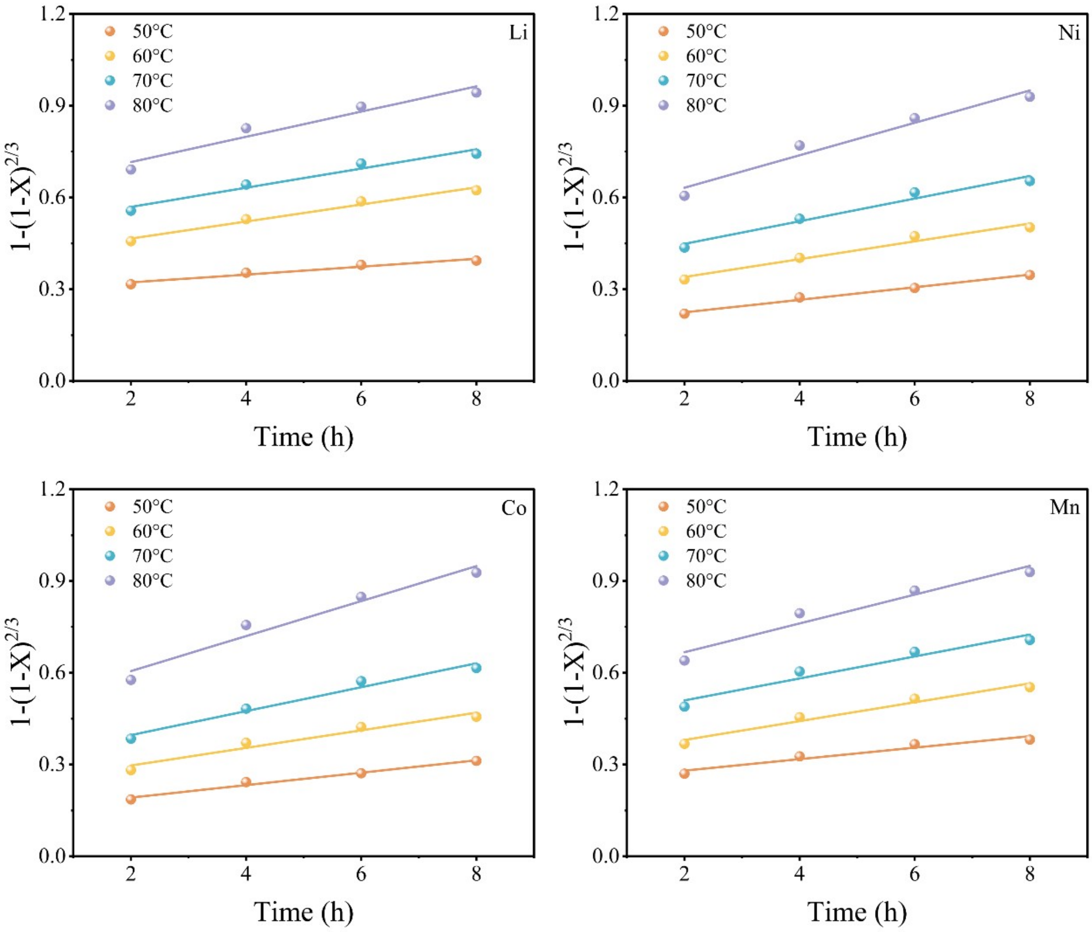


Figure S10 Fitting analysis of $1-(1-x)^{2/3}$ for Li, Ni, Co, and Mn in DES leaching system at different temperatures.

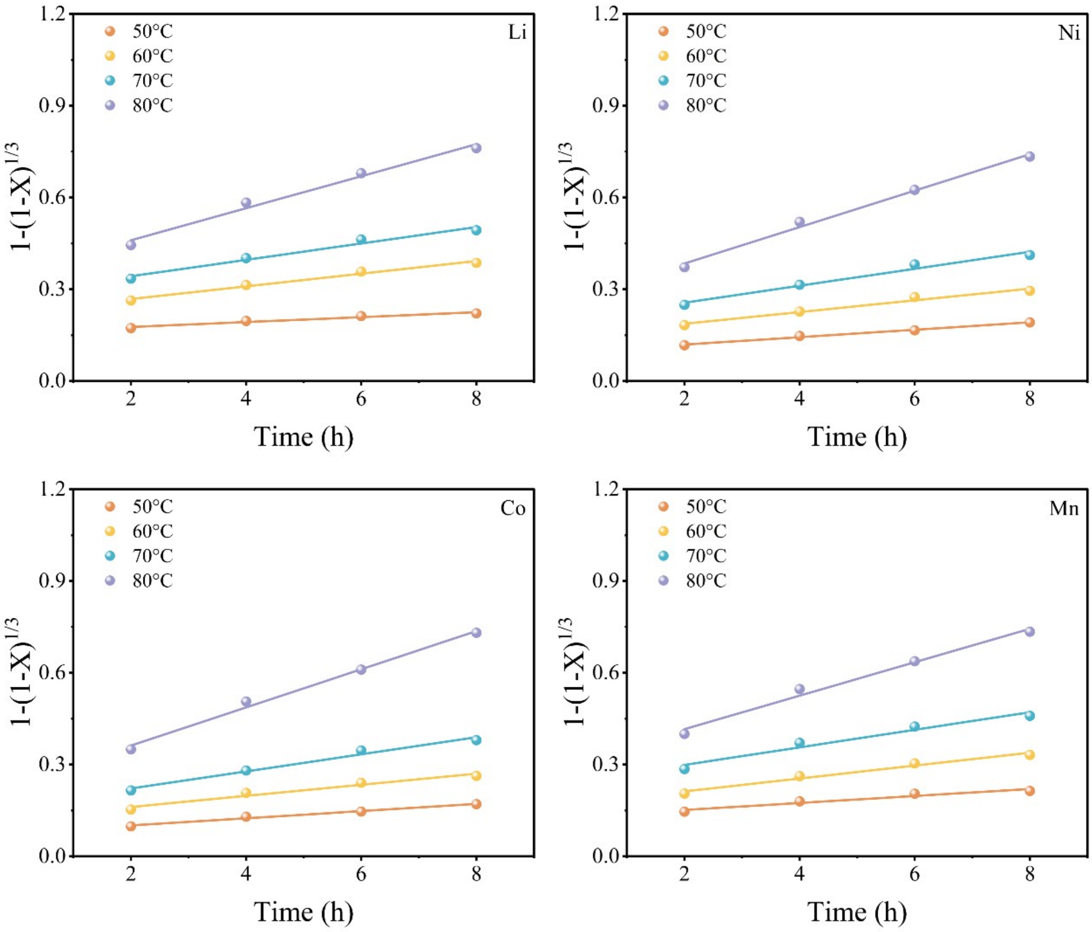


Figure S11 Fitting analysis of $1-(1-x)^{1/3}$ for Li, Ni, Co, and Mn in DES leaching system at different temperatures.

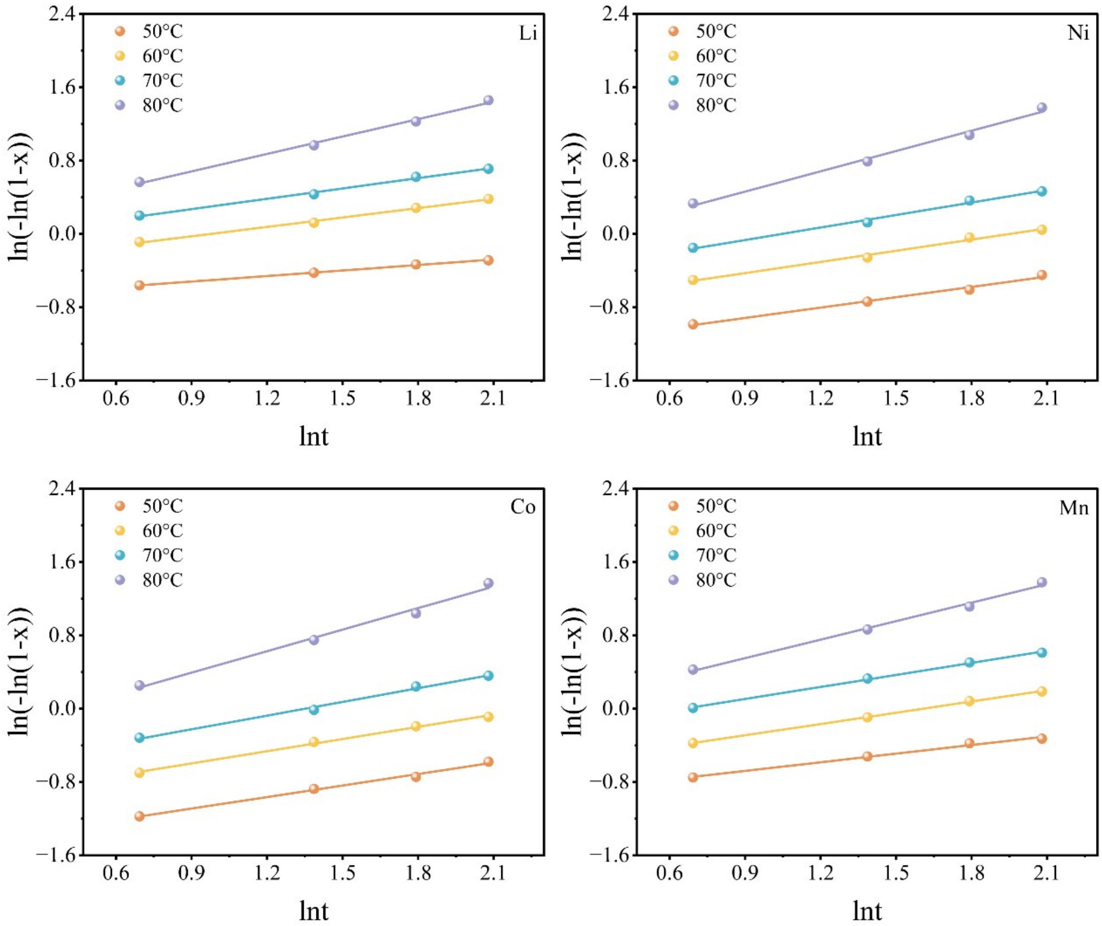


Figure S12 Avrami model fitting analysis of Li, Ni, Co, and Mn in DES leaching system at different temperatures.

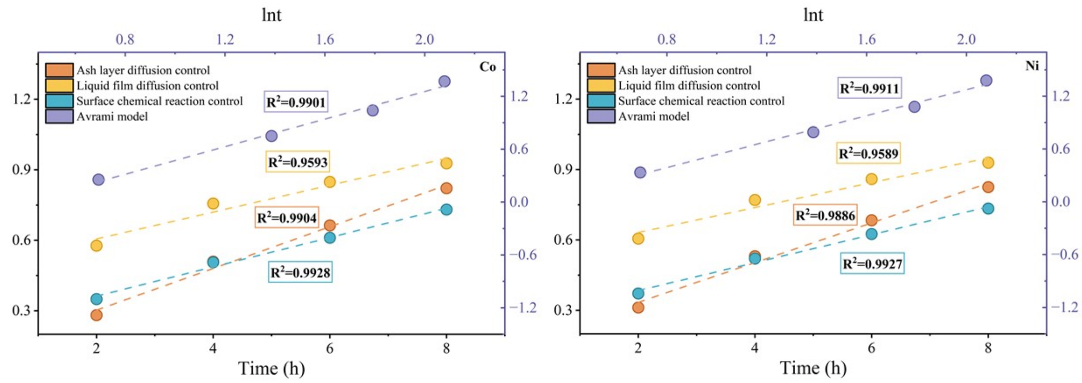


Figure S13 Comparison of kinetic models for Co and Ni.

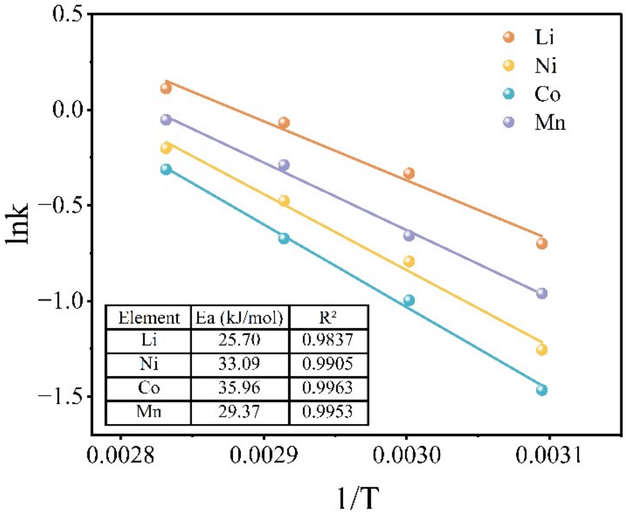


Figure S14 Arrhenius equation fitting results for Li, Ni, Co, and Mn in DES leaching system.

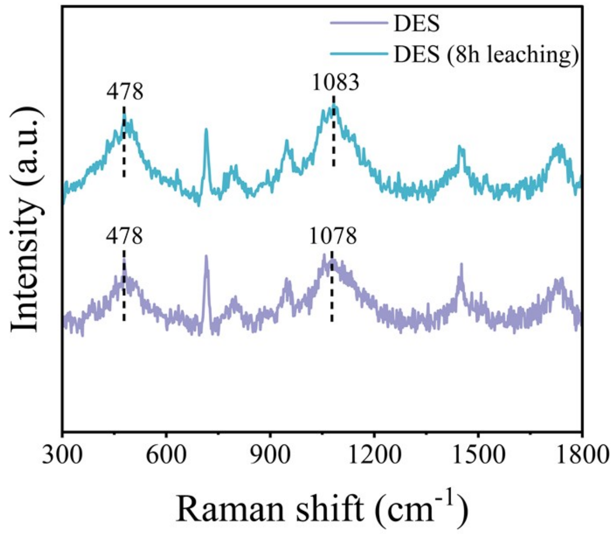


Figure S15 Raman spectra of raw DES and DES leachate.

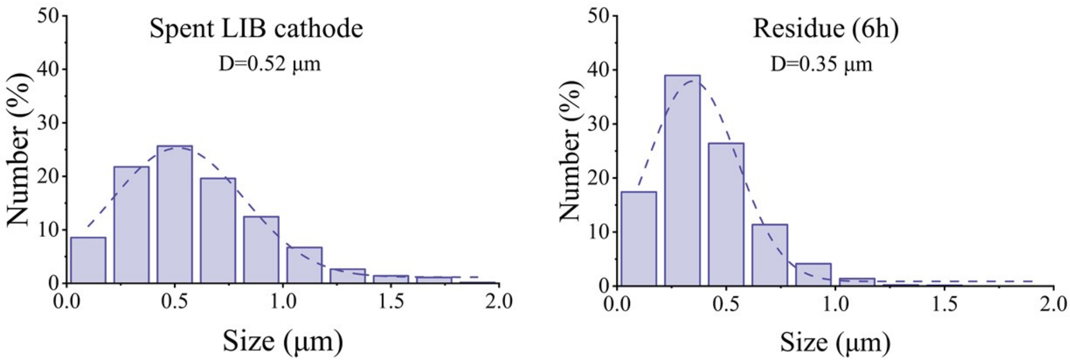


Figure S16 Particle size distribution of discarded LIB cathode and leachate residue after 6 h.

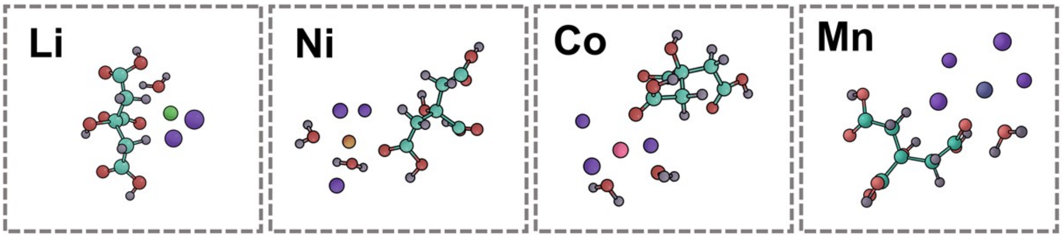


Figure S17 schematic coordination structures of different metals.

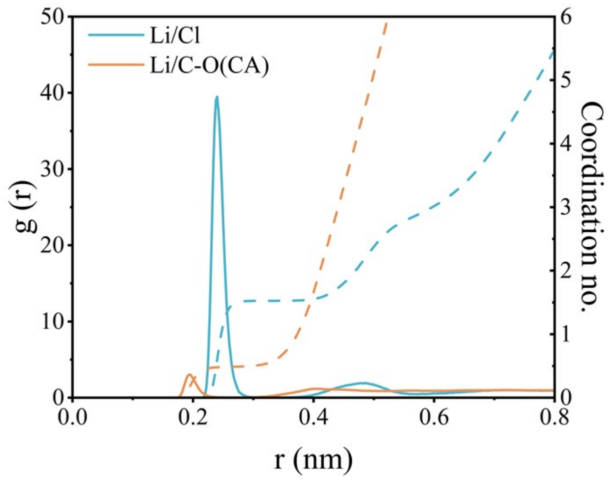


Figure S18 radial distribution functions (RDFs) of DES molecules around Li^{+}.

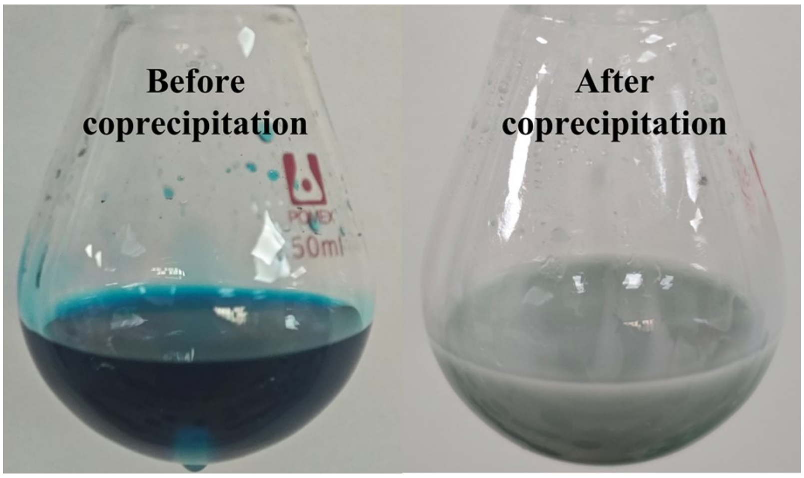


Figure S19 Digital images of DES leachate before and after coprecipitation.

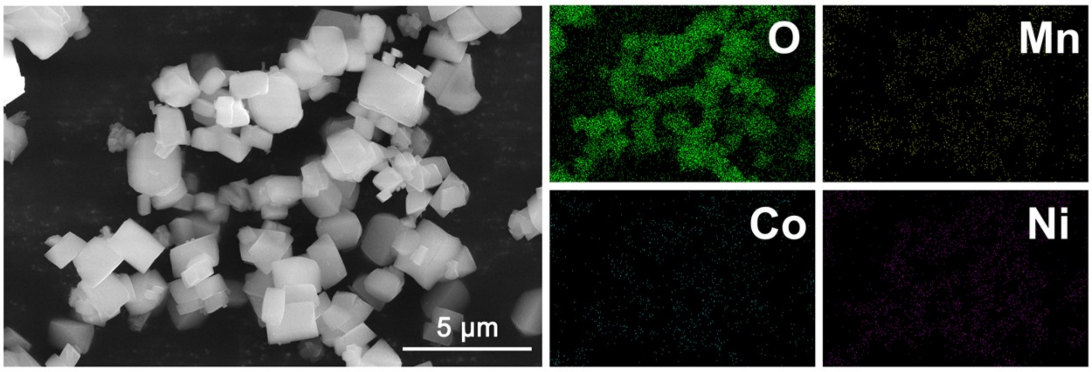


Figure S20 SEM image and EDS mapping of oxalate coprecipitation.

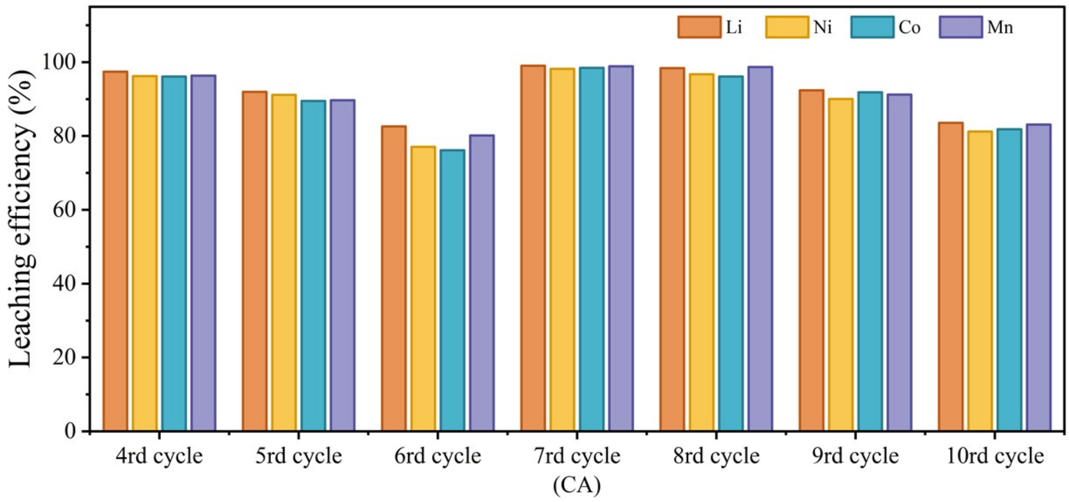


Figure S21 Cyclic leaching performance of the DES with CA supplementation.

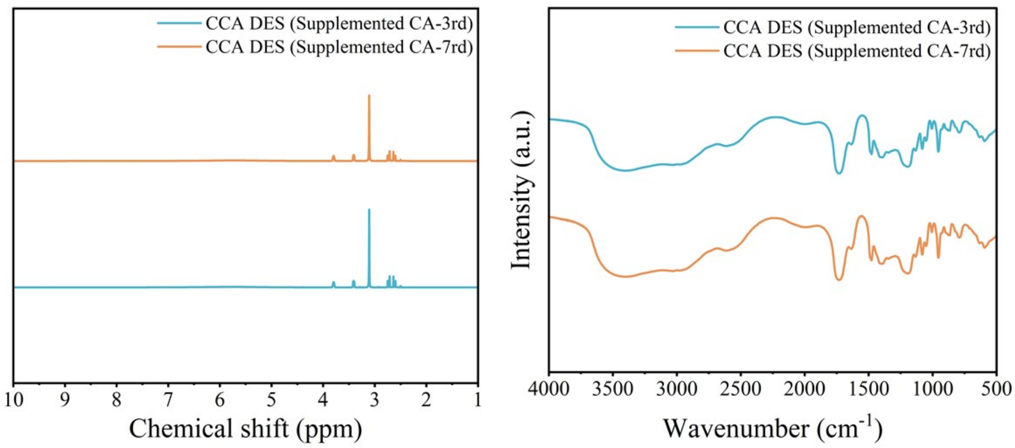


Figure S22 ^{1}H NMR spectra and FTIR spectra of DES (Supplemented CA).

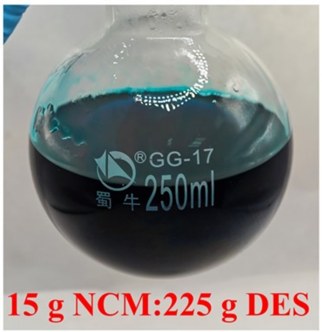
Gram-scale leaching tests	Metal	Leaching efficiency
	Li	99.07%
	Ni	98.68%
	Co	98.46%
	Mn	98.78%

Figure S23 Gram-scale leaching experiments.

Table S1 Acid dissociation constants (pKa) and VIP values of common organic acids

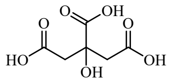
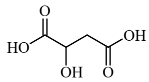
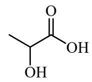
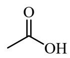
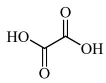
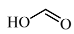
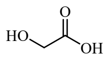
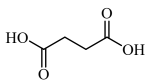
Acid	Structural formula	pK_a	VIP ($kJ \cdot mol^{-1}$)
Citric acid		3.09	922.97
Malic acid		3.45	907.77
Lactic acid		3.86	927.63
Acetic acid		4.76	1004.73
Oxalic acid		2.83	995.17
Formic acid		3.77	1063.77
Glycolic acid		3.83	961.91
Succinic acid		4.16	952.16

Table S2 Kinetic parameters for the leaching of Li, Ni, Co, and Mn at different temperatures using the unreacted shrinking core model.

Kinetics	Temperature(°C)	Li		Ni		Co		Mn	
		R^2	k	R^2	k	R^2	k	R^2	k
Ash layer diffusion control	323.15	0.96948	0.00764	0.99377	0.0095	0.99213	0.00817	0.95804	0.01014
	333.15	0.99090	0.02715	0.98173	0.02087	0.98000	0.01794	0.98709	0.02476
	343.15	0.97777	0.03877	0.98271	0.03658	0.98808	0.03484	0.97098	0.03995
	353.15	0.97203	0.07254	0.98863	0.08461	0.99042	0.08875	0.97955	0.0776
Liquid film diffusion control	323.15	0.95786	0.01287	0.99051	0.02056	0.98338	0.02032	0.94010	0.01871
	333.15	0.97918	0.02791	0.96997	0.02913	0.95406	0.02876	0.96843	0.03081
	343.15	0.96309	0.03133	0.96825	0.037	0.97357	0.03915	0.94563	0.03591
	353.15	0.94236	0.04127	0.95887	0.05301	0.95932	0.0572	0.94802	0.04708
Chemical reaction control	323.15	0.96091	0.00803	0.99198	0.01216	0.98569	0.01174	0.94444	0.01142
	333.15	0.98557	0.0207	0.97453	0.01917	0.96187	0.01818	0.97629	0.02109
	343.15	0.97420	0.02681	0.97664	0.02772	0.98122	0.02795	0.96173	0.02871
	353.15	0.98443	0.05231	0.99276	0.05951	0.99282	0.06239	0.98646	0.05467

Table S3 Avrami model fitting parameters for the leaching of Li, Ni, Co, and Mn at different temperatures.

Temperature (K)	Li			Ni			Co			Mn		
	R^2	lnk	n_c	R^2	lnk	n_c	R^2	lnk	n_c	R^2	lnk	n_c
323.15	0.99803	-0.69957	0.20061	0.99066	-1.25484	0.37631	0.99365	-1.46518	0.41816	0.99169	-0.96029	0.31369
333.15	0.99633	-0.33236	0.34119	0.99104	-0.79325	0.40671	0.99632	-0.99546	0.44346	0.99951	-0.65808	0.40948
343.15	0.99522	-0.06778	0.37614	0.99301	-0.47581	0.45501	0.99425	-0.67299	0.4984	0.99827	-0.28854	0.4385
353.15	0.99536	0.11174	0.63407	0.99114	-0.20127	0.73743	0.99006	-0.31076	0.78266	0.99384	-0.05249	0.67188

Table S4 XRD refinement parameters of NCM523 and Residue (6 h).

Sample	c/a	Li/Ni (%)	I_{003}/I_{104}	R_{wp}	Chi2
NCM523	4.9595	11.8	2.06	5.72	2.63
Residue(6h)	4.9541	20	1.10	6.07	2.97

Table S5 Atomic percentage of Ni 2p, Co 2p, and Mn 2p on the surface of NCM523 and various leaching residues at different times.

Sample	Ni^{3+}/Ni^{2+}	Co^{3+}/Co^{2+}	Mn^{4+}/Mn^{2+}
NCM523(0h)	57.79/42.21	60.73/39.28	31.14/68.86
Residue(2h)	49.56/50.44	56.19/43.82	28.40/71.60
Residue(4h)	31.68/68.32	48.94/51.05	20.63/79.37
Residue(6h)	22.68/77.32	42.04/57.97	0/100.00

Table S6 Theoretical citric acid supplement calculated from the total electron requirement for NCM reduction

Cycles	Mass (g)	Leaching efficiencies (%)			The number of electrons required for NCM reduction (mol)	CA consumption (g)	CA supplement (g)
		Ni	Co	Mn			
0	0.2	98.12	98.05	98.13	0.0020	0.2135	
1	0.2	97.42	97.17	97.60	0.0020	0.2121	
2	0.2	80.36	79.87	82.27	0.0017	0.1772	0.6028
3	0.2	97.73	97.44	98.01	0.0020	0.2129	
4	0.2	96.22	96.11	96.33	0.0020	0.2095	
5	0.2	91.15	89.47	89.66	0.0019	0.1957	
6	0.2	77.06	76.13	80.12	0.0016	0.1713	0.7894

Calculation instructions:

Reaction equation:

$$2LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 + C_6H_8O_7 + 6H^+ \rightarrow 2Li^+ + Ni^{2+} + 0.4Co^{2+} + 0.6Mn^{2+} + C_5H_6O_5 + CO_2 + 4H_2O$$

Calculated based on the total number of electrons required for reduction:

$$m_{CA} = \frac{n_{e^-}}{2} \times M_{CA} = \frac{n_{NCM} \times (0.2\eta_{Ni} + 0.2\eta_{Co} + 0.6\eta_{Mn})}{2} \times M_{CA}$$

where m_{CA} is the mass of CA consumed (g), n_{e-} is the number of electrons required for NCM reduction (mol), M_{CA} is the molar mass of CA, n_{NCM} is the amount of NCM required (mol), η is the leaching efficiency of each metal.

Table S7 Comparison with previously reported DES systems.

DES	Temperature (°C)	Solid-liquid ratio (g/L)	Leaching efficiency (%)
CPL+UR+FA	120	20	Li(93.4), Ni(87.8), Co(89.6), Mn(90.1)
EG+CA	150	20	Li(99.99), Ni(99.86), Co(100.00), Mn(99.93)
EG+GA	140	26	Li(92.61), Ni(91.67), Co(90.04), Mn(94.17)
ChCl+PA	100	11.11	Li(97.7), Ni(96.4), Co(97.0), Mn(93.0)
BeCl+FA	140	20	Li(98.03), Ni(92.35), Co(94.19), Mn(96.01)
This work	80	103.33	Li(98.64), Ni(98.12), Co(98.05), Mn(98.13)

CPL: caprolactam, UR: urea, FA: formic acid, EG: ethylene glycol, GA: gluconic acid, PA: phenylphosphinic acid, BeCl: betaine hydrochloride.

To ensure the fairness and accuracy of the comparison, the solid-liquid ratio of all DES systems was uniformly converted to the same unit. The density of DES in this study is 1.55 g/ml.

Table S8 Life cycle analysis of Pyrometallurgical recycling.

Procedures	Input	Amount	Output	Amount	Notes
Discharging & Crushing	**Spent LIBs**	1.0 t	**Spent LIBs (100% SOD)**	1.0 t	1 MJ electricity produces 0.13 kg GHG and 0.67 L water. 1 kg diesel produces 45.6 MJ energy. The data is estimated based on Everbatt 2023. 5 wt% NaCl solution is used for the discharging process.[1-3]
	Energy	30 MJ	GHG	4 kg	
	Water	520 L			
	NaCl	0.3 kg			
Smelting	**Spent LIBs (100% SOD)**	1.0 t	**Matte (Co, Ni, Mn, Fe, Cu)**	0.4 t	The purpose is to reduce the transition metals and remove all the impurities. The by products include the slag with Al, Ca and Li, which requires the post-treatment to recycle the Li salts. The temperature is ~1873 K for 3 h.
	SiO_2/CaO mixture	0.3 t	Slag (Li, Al, Ca-contained)	0.41 t	
	Energy	10700 MJ	GHG	1400 kg	
	Water	7169 L			
Gas treatment	Energy	1300 MJ	GHG	170 kg	
	Water	870 L			
Refine	**Matte**	0.4 t	**Metal alloy**	~0.30 t	
	Energy	3 MJ	GHG	0.4 kg	
	Water	2 L	Cu	0.08 t	

Table S9 Life cycle analysis of Hydrometallurgical recycling.

Procedures	Input	Amount	Output	Amount	Notes
Discharging & Disassembly	**Spent LIBs**	1.00 t	**NCM523 cathode**	0.48 t	The data is estimated based on Everbatt 2023. 5 wt% NaCl solution is used for the discharging process.[1,2] 1 MJ electricity produces 0.13 kg GHG and 0.67 L water. 1 kg diesel produces 45.6 MJ energy.
	Energy	30 MJ	GHG	4 kg	
	Water	520 L			
	NaCl	0.3 kg			
Thermal treatment	**NCM523 cathode**	0.48 t	**NCM523 Powder**	0.35 t	The purpose is to separate the active materials with current collectors, to decompose the binder, electrolyte residue and SEI components. The temperature is ~873 K for 2 h.[4]
	Energy	2900 MJ	Al foil	0.1 t	
			GHG	377 kg	
Acid leaching	**NCM523 Powder**	0.35 t	**Leachate**	12.8 t	Leaching conditions: H_2SO_4 =2 mol/L, 3% H_2O_2, stirring speed=400 rpm, pulp density=50 g/L, and T=60 °C, 1 hour.[5] Concentrated H_2SO_4 is 1.84 g/mL. 30% H_2O_2 is ~1.11 g/mL
	Energy	2100 MJ	GHG	273 kg	
	Water	10810 L			
	98% H_2SO_4	743 L			
	H_2O_2	204 L			
Chemical precipitation	**Leachate**	12.8 t	**Compounds (Ni, Co and Mn)**	13.34 t	The solution degree of Na_2CO_3 is 40 g/100g (30 °C). Reaction 6 h.
	Na_2CO_3	193 kg	**Li_2CO_3**	134 kg	
	Energy	1150 MJ	GHG	150 kg	
	Water	483 L			

Table S10 Life cycle analysis of this work

Procedures	Input	Amount	Output	Amount	Notes
Discharging & Disassembly	**Spent LIBs**	1.00 t	**NCM523 cathode**	0.48 t	1 MJ electricity produces 0.13 kg GHG and 0.67 L water. 1 kg diesel produces 45.6 MJ energy. The data is estimated based on Everbatt 2020. ~5 wt% NaCl solution is used for the discharging process.
	Energy	30 MJ	GHG	4 kg	
	Water	520 L			
	NaCl	0.3 kg			
Thermal treatment	**NCM523 cathode**	0.48 t	**NCM523 Powder**	0.35 t	The purpose is to separate the active materials with current collectors, to decompose the binder, electrolyte residue and SEI components. The temperature is ~873 K for 2 h.[4]
	Energy	2900 MJ	GHG	377 kg	
			Al foil	0.1 t	
DES leaching	**NCM523 Powder**	0.35 t	**Leachate**	2.7 t	DES recycling
	Energy	2190 MJ	GHG	285 kg	
	Water	896 L			
	choline chloride	580 kg			
	CA H_2O	872 kg			
Chemical precipitation	**Leachate**	2.7 t	**oxalic acid co-precipitation**	0.52 t	
	Oxalic acid	394 kg	**Li solution**	2.18 t	
	Energy	210 MJ	GHG	28 kg	
	Water	3500 L			

Table S11 The specific price of different materials involved.

Materials	Prices ($/t)
Spent Lithium-ion battery	2139
H_2SO_4	212
H_2O_2	283
Na_2CO_3	354
NaCl	43
choline chloride	354
CA H_2O	425
Oxalic acid	283
Li_2CO_3	8076
Li salt	3256
Al foil	2123
Cu	2194
oxalic acid co-precipitation	7637
Metal alloy	9910

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