Ultra-High Efficient Lithium Recovery via Terephthalic Acid from Spent Lithium-ion Batteries

Jiahui Hou[1,3], Zexin Wang[1,3], Zifei Meng[1], Jinzhao Fu[1], Zeyi Yao[1], Wenting Jin[1], Xiaotu Ma[1], Zhenzhen Yang[2], Yan Wang[1*]

[1] Department of Mechanical and Materials Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, USA

[2] Chemical Science & Engineering, Argonne National Laboratory, 9700 S Cass Ave, Lemont, IL 60439, USA

[3] These authors contributed equally.

[*] Corresponding: yanwang@wpi.edu

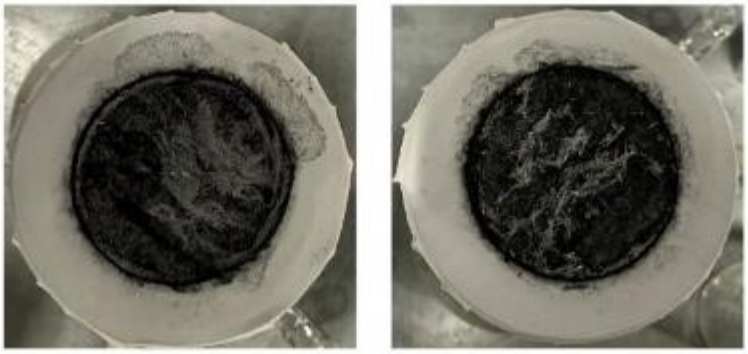

Figure S1 The morphology of TPA under different temperature

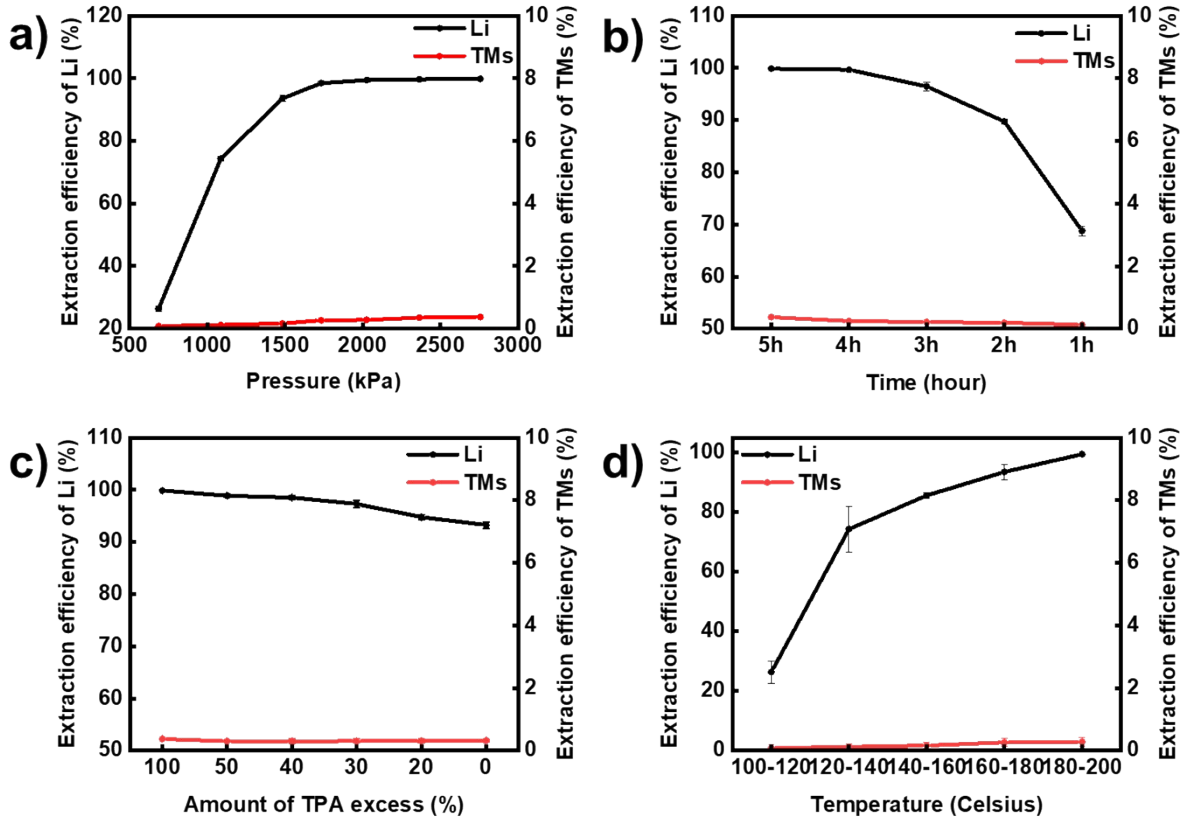

Figure S2 The extraction efficiency for lithium and impurity from NMC622 under a) different pressure, b) different time, c) different amount of TPA excess, and d) different temperature.

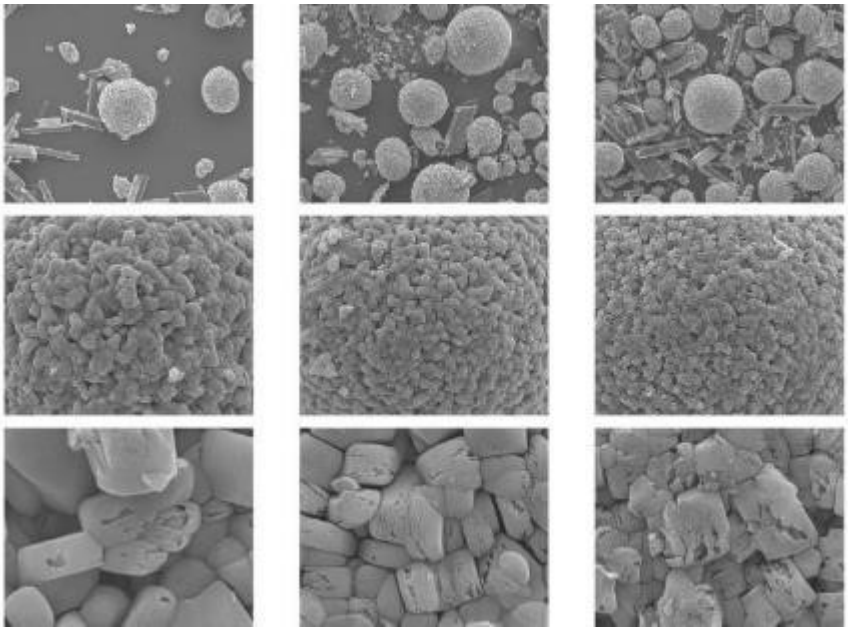

Figure S 3 The SEM for powder after extraction reaction with different pressure.

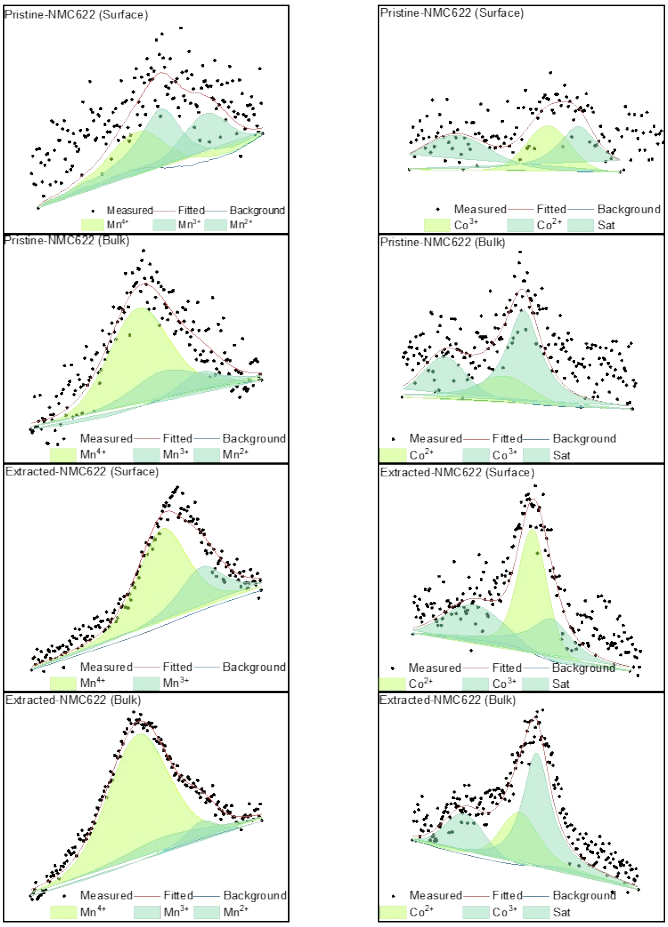

Figure S 4 XPS for Mn, Co

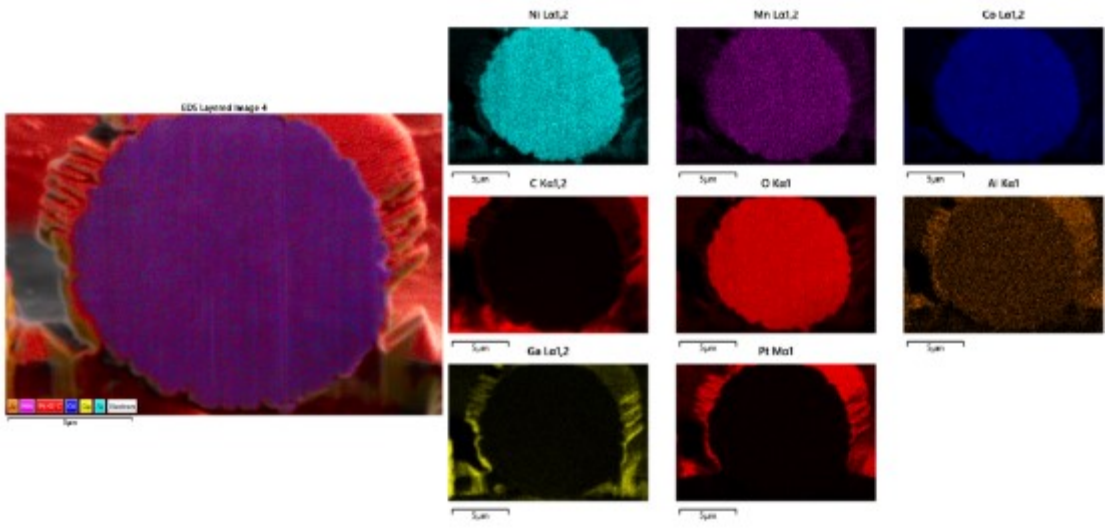

Figure S 5 The EDS mapping for virgin NMC622 cathode powder.

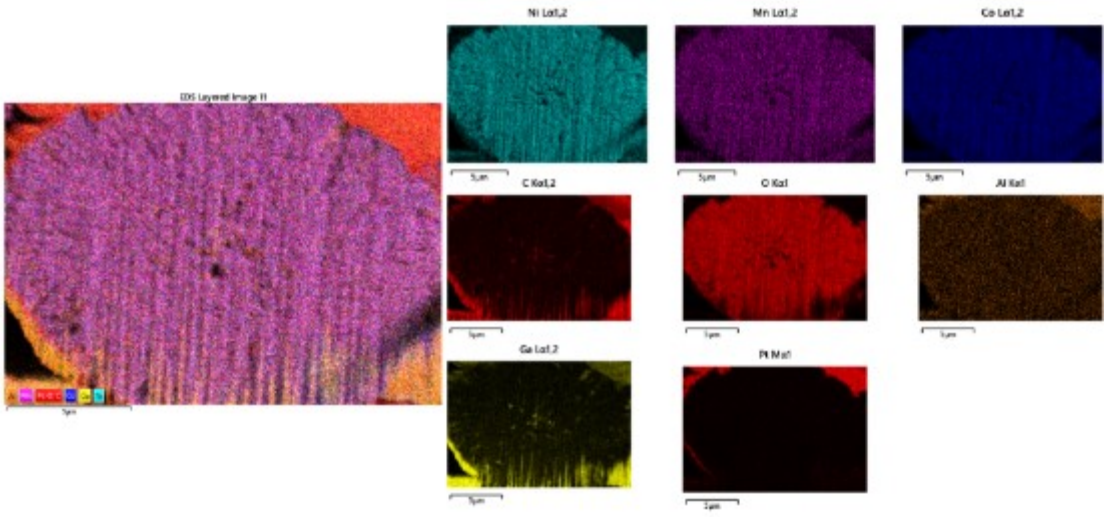

Figure S 6 The EDS mapping for extracted NMC622 cathode powder.

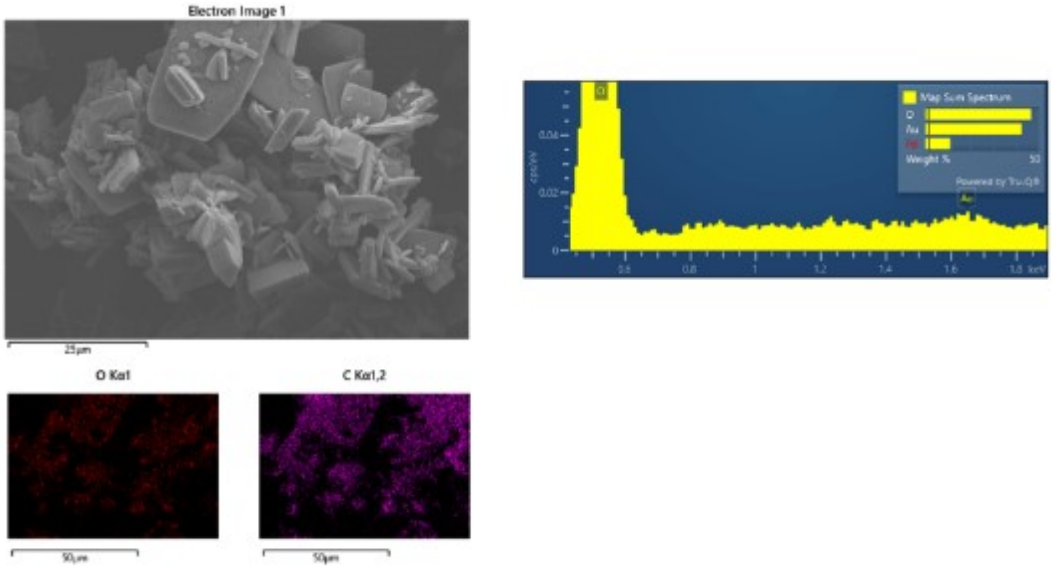

Figure S 7 EDS mapping for Li_2TP.

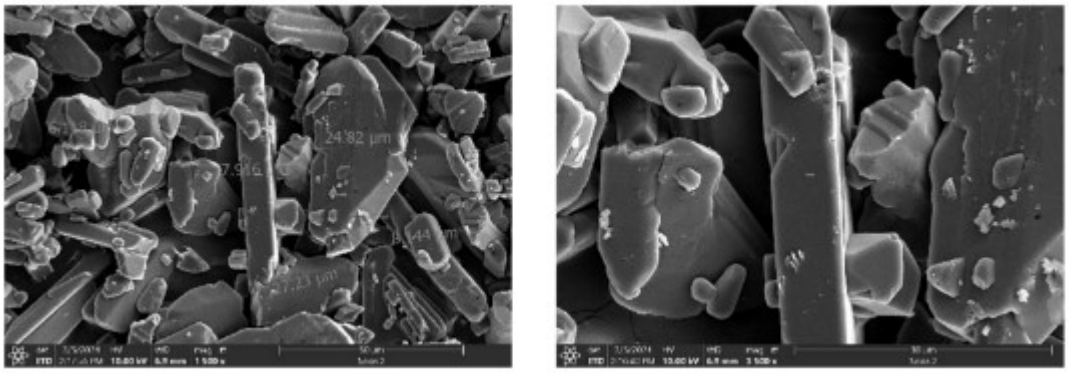

Figure S 8 The morphology for commercial lithium carbonate.

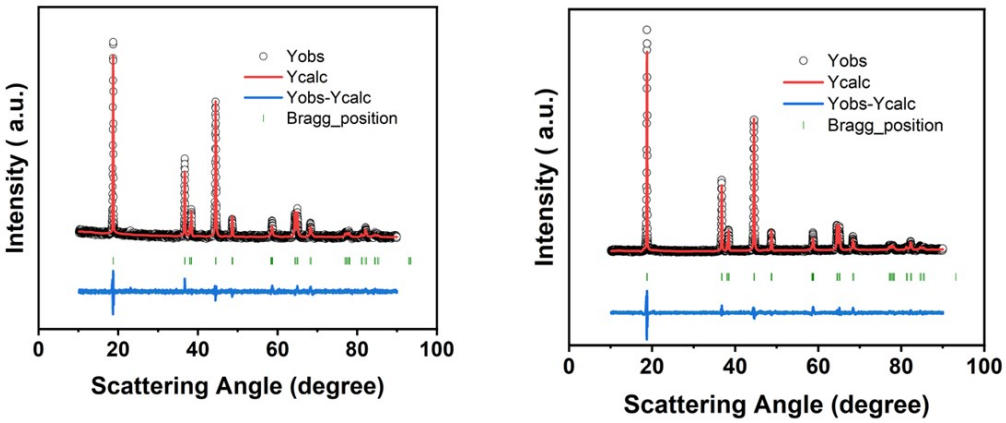

Figure S9 XRD refinement for V-NMC622 and R-NMC622

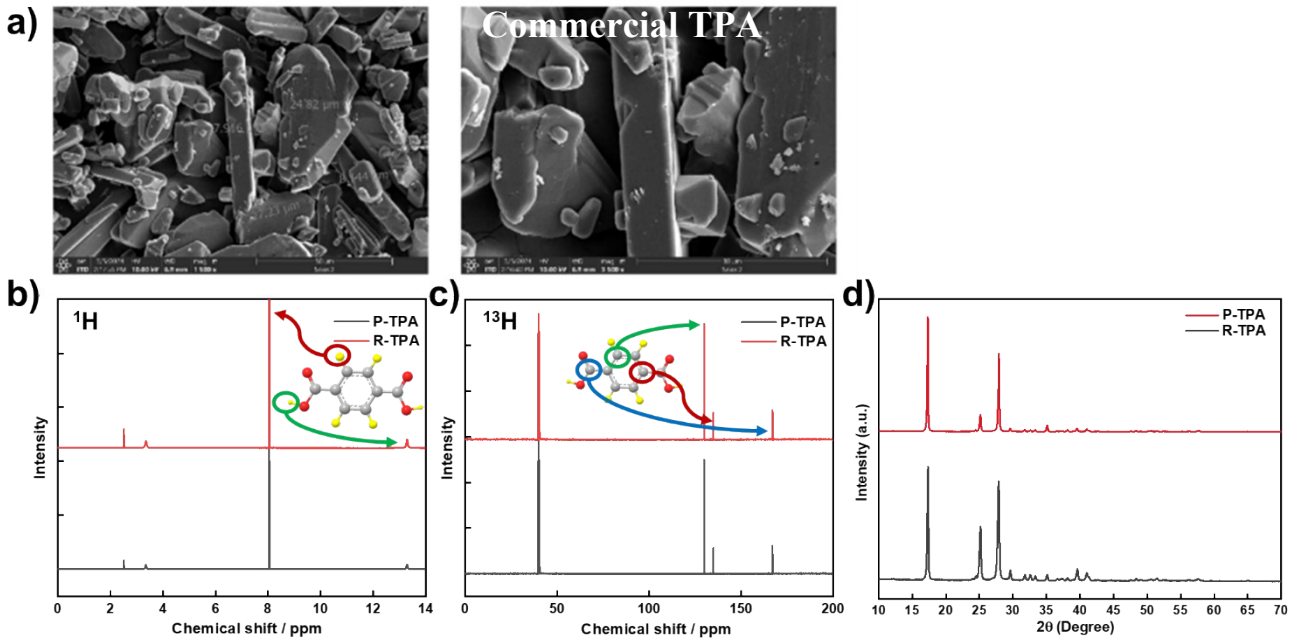

Figure S10 a)SEM images for recovered TPA and commercial TPA, b) 1H NMR comparison for pristine (P-TPA) and recycled TPA (R-TPA), c) 13C NMR comparison for P-TPA and R-TPA, d) XRD comparison for P-TPA and R-TPA.

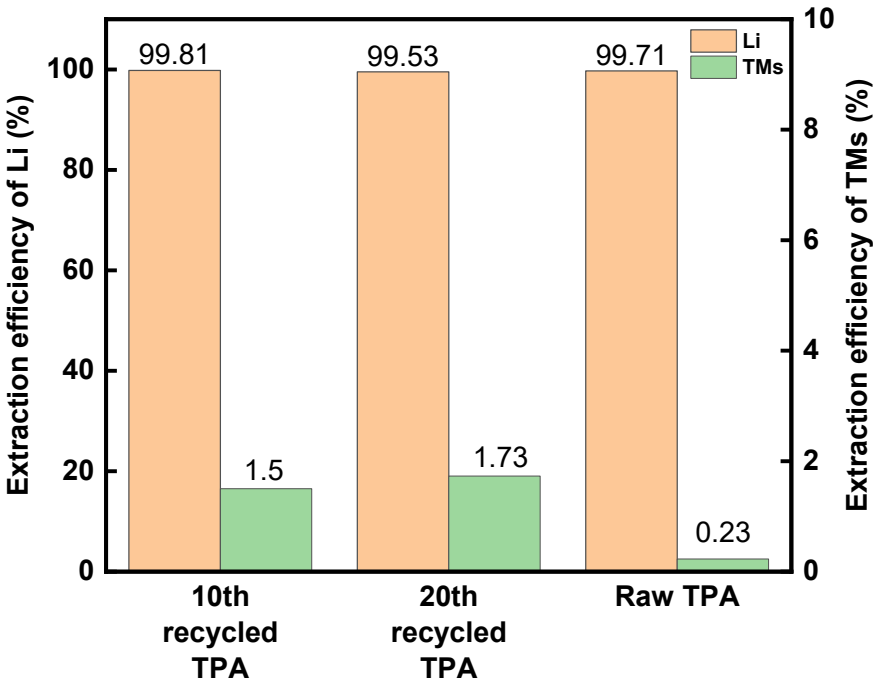

Figure S11 Extraction efficiency comparison for used TPA and raw TPA.

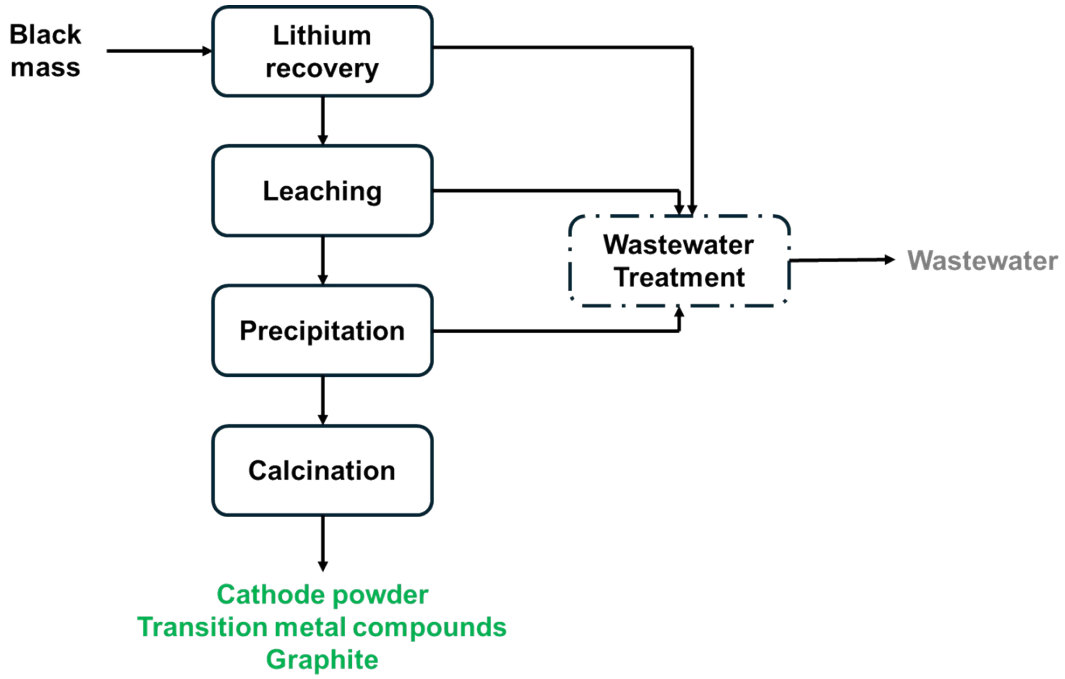

Figure S12 Process diagram of a TPA-lithium recovery process. Solid boxes denote common unit operations; dashed box denotes optional unit operation; green denotes products; grey denotes wastes.

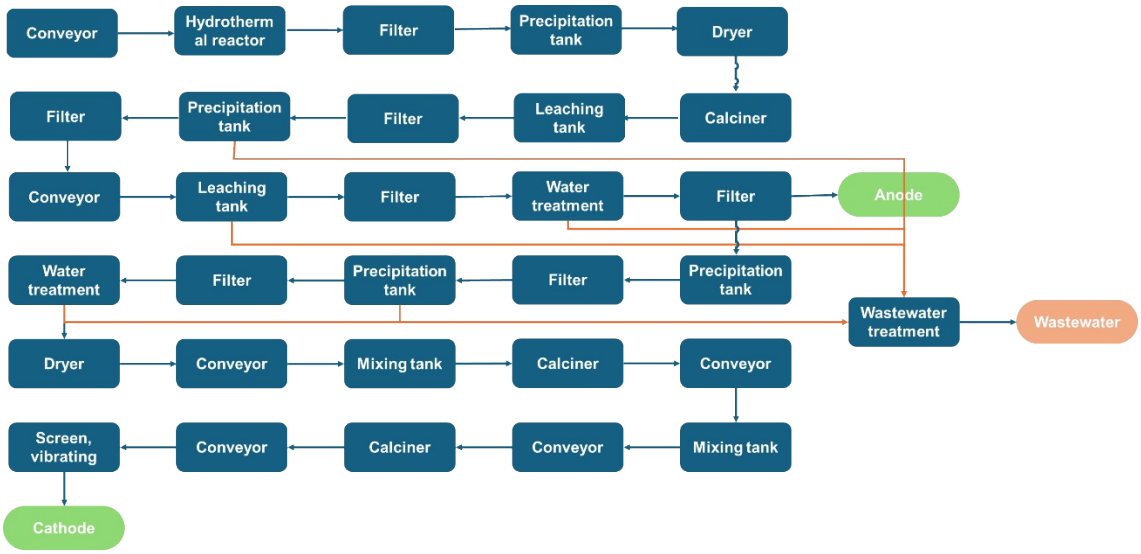

Figure S13 Detailed process and equipment usage for TPA-lithium recovery process.

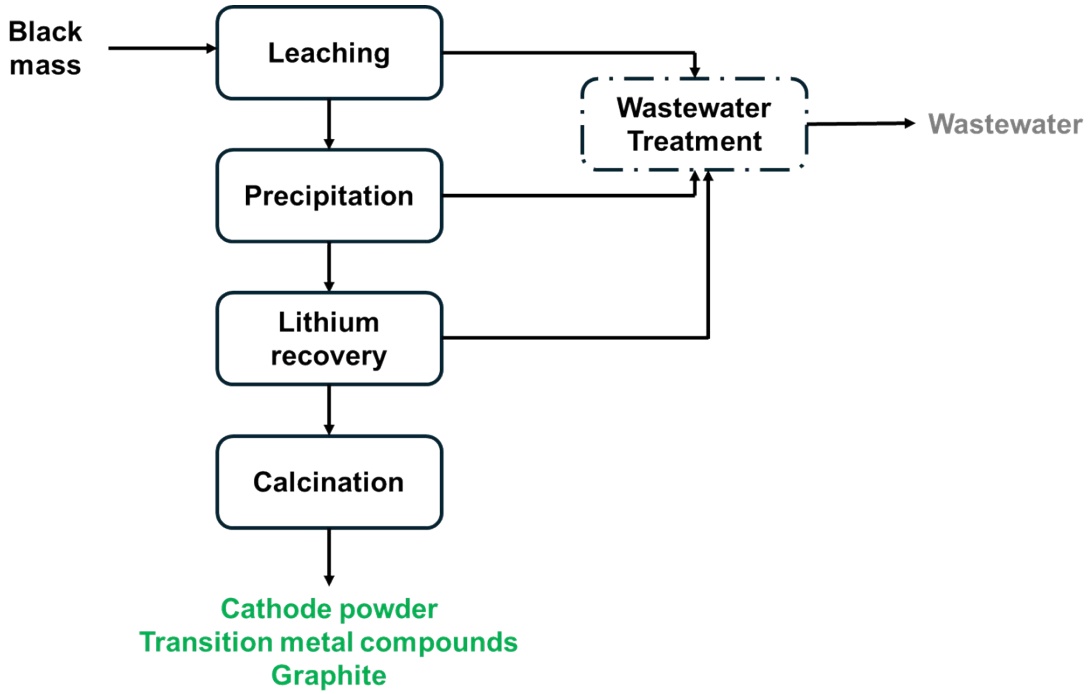

Figure S14 Process diagram of a traditional lithium recovery process. Solid boxes denote common unit operations; dashed box denotes optional unit operation; green denotes products; grey denotes wastes.

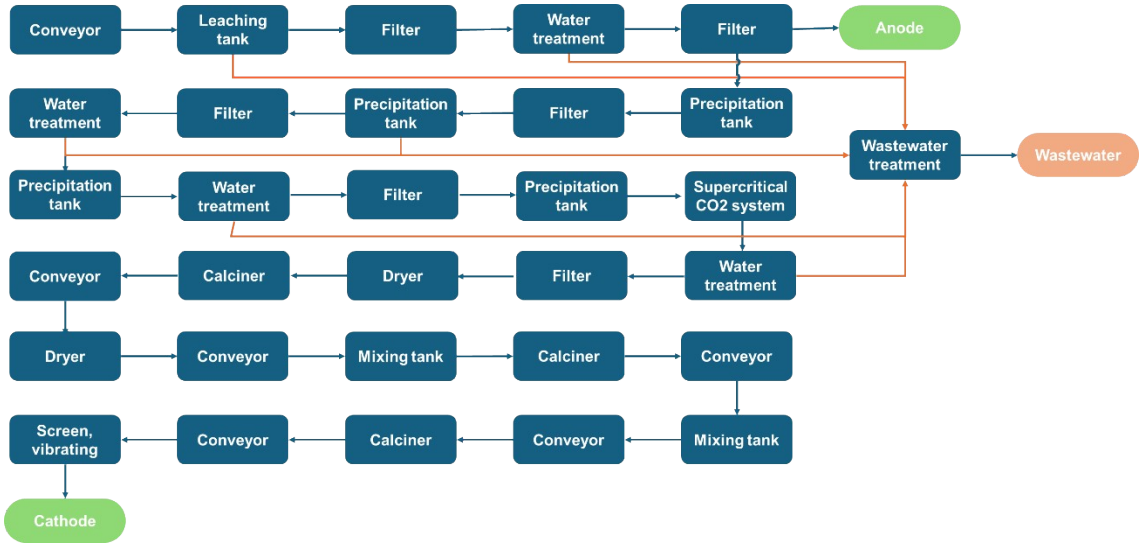

Figure S15 Detailed process and equipment usage for traditional lithium recovery process.

Table 1 Summarized stoichiometric elemental ratio obtained from ICP-OES analysis for different raw materials

Sample ID	Li	Ni	Mn	Co	Fe	P
NMC622	1.02	0.6	0.2	0.2	-	-
LMO	1.01	-	2	-	-	-
LCO	1.03	-	-	1	-	-
LFP	1.03	-	-	-	1.0	1
Black mass	0.83	0.21	0.57	0.22	0.2wt%	-

Table 2 The detailed information for repeatable data

Pressure	Li	TMs	Time	Li	TMs	TPA%	Li	TMs
685.325	26.14	0.09	5h	99.84	0.36	100%	99.84	0.36
	25.31	0.05		100	0.38		100	0.38
	27.52	0.1		99.71	0.37		99.71	0.37
Mean	26.32	0.08	Mean	99.85	0.37	Mean	99.85	0.37
Standard Deviation	0.79	0.02	Standard Deviation	0.10	0.01	Standard Deviation	0.10	0.01
1085.95	74.76	0.12	4h	99.64	0.23	50%	99.01	0.31
	73.21	0.1		99.81	0.3		98.35	0.26
	75.03	0.13		99.53	0.2		99.21	0.33
Mean	74.33	0.12	Mean	99.66	0.24	Mean	98.86	0.30
Standard Deviation	0.69	0.01	Standard Deviation	0.10	0.04	Standard Deviation	0.32	0.03
1483.01	93.01	0.18	3h	96.44	0.2	40%	98.53	0.3
	92.53	0.16		95.31	0.18		98.02	0.2
	95.21	0.14		97.62	0.26		99.01	0.4
Mean	93.58	0.16	Mean	96.46	0.21	Mean	98.52	0.30
Standard Deviation	1.01	0.01	Standard Deviation	0.82	0.03	Standard Deviation	0.35	0.07
1732.54	98.96	0.27	2h	89.98	0.19	30%	97.5	0.31
	97.53	0.21		89.03	0.15		96.31	0.21
	99.02	0.3		90.16	0.23		98.05	0.4
Mean	98.50	0.26	Mean	89.72	0.19	Mean	97.29	0.31
Standard Deviation	0.60	0.03	Standard Deviation	0.43	0.03	Standard Deviation	0.63	0.07
2025.07	99.35	0.27	1h	69.85	0.16	20%	94.94	0.32
	100	0.35		67.23	0.1		94.01	0.21
	99.01	0.21		69.16	0.12		95.34	0.4
Mean	99.45	0.28	Mean	68.75	0.13	Mean	94.76	0.31
Standard Deviation	0.36	0.05	Standard Deviation	0.96	0.02	Standard Deviation	0.48	0.07
2363.6	99.53	0.31				0%	93.36	0.35
	100	0.38					92.34	0.25
	99.61	0.35					94.01	0.36
Mean	99.71	0.35				Mean	93.24	0.32
Standard Deviation	0.18	0.02				Standard Deviation	0.60	0.04
2757.13	99.84	0.36						
	100	0.38						
	99.71	0.37						
Mean	99.85	0.37						
Standard Deviation	0.10	0.01						

Table 3 Detailed calculation information for pressure.

temperature	saturated vapor pressure	Volume expansion	Total pressure
T1	198.97	486.36	685.33
T2	478	607.95	1085.95
T3	794	689.01	1483.01
T4	1003	729.54	1732.54
T5	1255	770.07	2025.07
T6	1553	810.6	2363.60
T7	1906	851.13	2757.13

Table 4 Detailed calculation for excess of TPA.

Excess of TPA	Base TPA
0%	MLi*1*MWTPA
20%	MLi*1.2*MWTPA
30%	MLi*1.3*MWTPA
40%	MLi*1.4*MWTPA
50%	MLi*1.5*MWTPA
100%	MLi*2*MWTPA

*MLi=mol of lithium in CAM

*MWTPA=molar weight of TPA

Table S5 ICP results for extracted-NMC622 and Li_2TP powder.

Sample ID	Li	Ni	Mn	Co
Pristine NMC622	1.02	0.6	0.2	0.2
Extracted NMC622	0.0005	0.6	0.2	0.2
Li_2TP (mg/kg)	74,970.6	1832.1	615.2	673.5

Table 6 XRF test results for commercial Li_2CO_3 and recovered Li_2CO_3

	XRF test results (mg/kg)													
	Mg	**Al**	**Si**	**P**	**S**	**Ca**	**Ti**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Purity%**
C-Li_2CO_3	4620	1364	/	/	318	210	/	48	3438	104	/	19	71	98.97%
R-Li_2CO_3	/	1253	261	/	825	914	228	129	1456	/	22	25	29	98.77%

Table 7 ICP test results for commercial Li_2CO_3 and recovered Li_2CO_3

	ICP test results (mg/kg)													
	Mg	**Al**	**Si**	**P**	**S**	**Ca**	**Ti**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Purity%**
C-Li2CO3	12	206	788	126	280	/	/	30	92	8	38	/	38	**99.84%**
R-Li2CO3	28	132	392	118	216	/	/	22	50	8	30	/	28	**99.90%**

Table 8 Detailed structure from XRD refinement

	a-axis	c-axis	Volume	Ni in Li layer	$\chi 2$	Rwp
V-NMC622	2.86610	14.20194	101.033	3.66%	3.91	2.3
R-NMC622	2.87069	14.23199	101.571	3.66%	1.56	3.67

Table S9 ICP-OES test results for recovered TPA.

	Mg	Al	P	S	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Purity%
C-TPA	40	254	90	74	/	/	32	40	18	46	/	54	99.82%
1st R-TPA	52	228	92	490	/	/	130	52	118	382	/	38	98.79%
20th R-TPA	48	237	90	512	/	/	127	46	107	468	/	45	98.81%

Table S 10 The comparison of TPA-lithium recovery process with other organic acids.

	Li%	TMs%	Mechanism	Note	Reference
Oxalic acid	98.8%	<1.5%	Trace soluble of transition metal oxalate	The Al will be fully dissolved with Li	24
Formic acid	>99%	<5%	Trace soluble transition metal formate in the concentrated formic acid	The ratio of transition metal formate was over 20% in the residue powder.	25
Citric acid	>95%	>95%	Dissolve all metals in the citric acid	Further solvent extraction method needed to separate transition metals.	19-23
TPA	>98%	<1%	Trace soluble transition metal terephthalate	A universal method for LMO, LCO, LFP and NMC cathode powder.	This work