Green and Economic Lithium Recovery from Spent $LiMn_2O_4$ Batteries through Blue Vitriol-Driven Selective Sulfation Roasting

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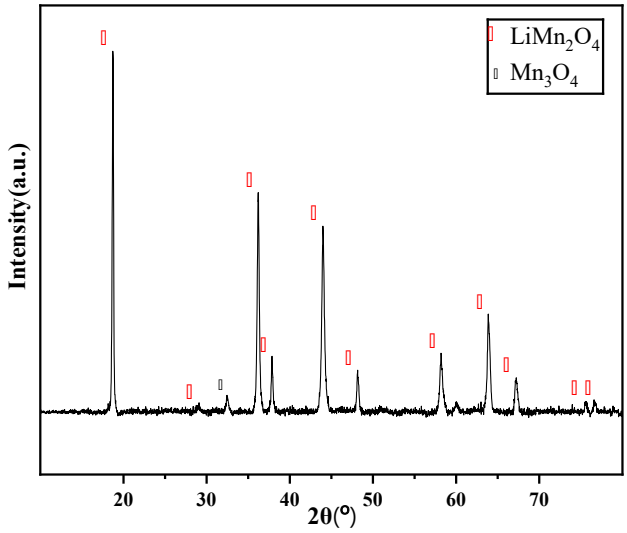

Figure S1. XRD pattern of spent LMO cathode.

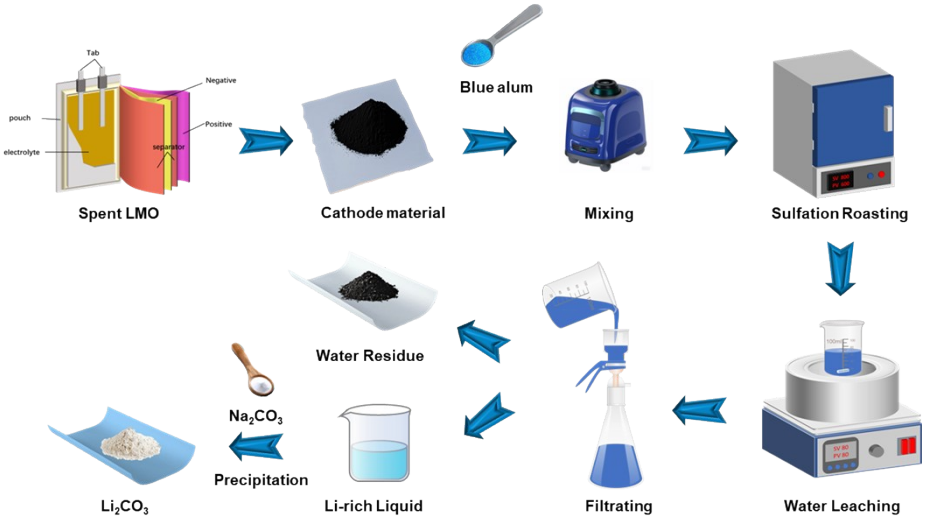

Figure S2. Process flow diagram of selective lithium recovery from spent LMO battery.

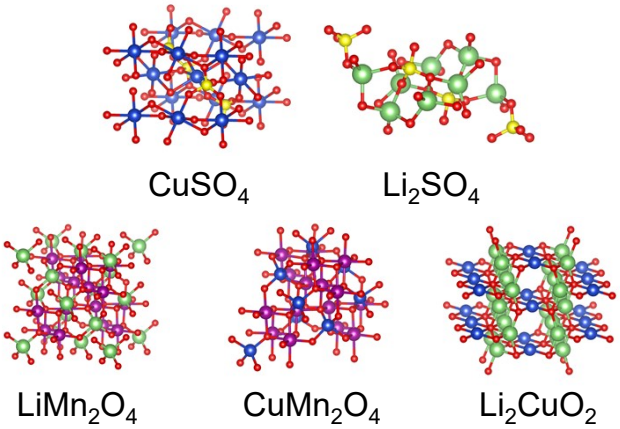

Figure S3. Modeling results of $CuSO_4$, Li_2SO_4, $LiMn_2O_4$, $CuMn_2O_4$, Li_2CuO_2.

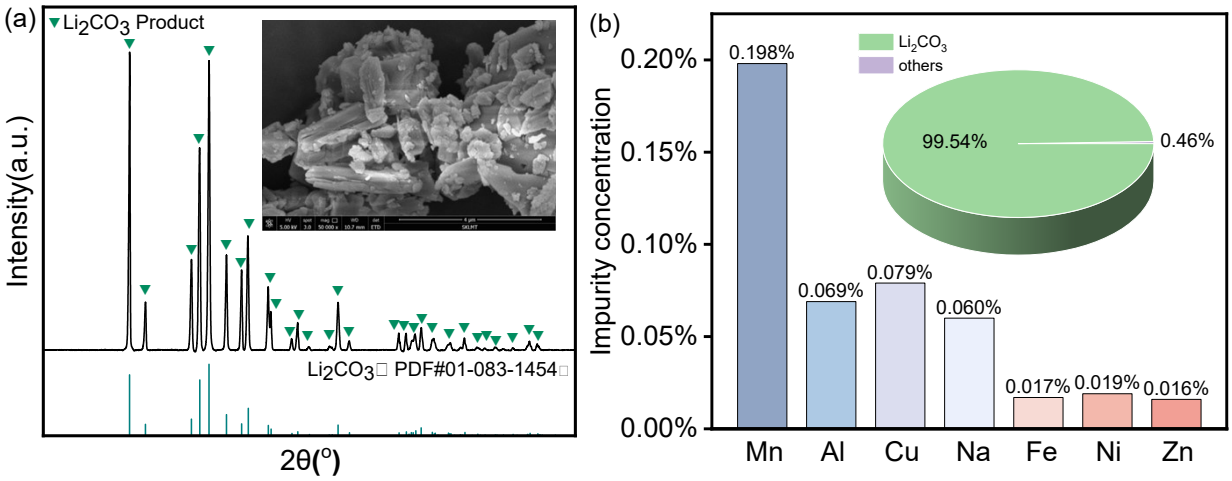

Figure S4. (a) Characterizations of the recovered Li_2CO_3, (b) Elemental composition of the recovered Li_2CO_3.

Table S1. XRF results of spent LMO cathode.

Composition	MnO	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	Fe_2O_3	NiO	other
Cathode powder	97.338	0.4793	0.0395	0.5018	0.7689	0.0431	0.2745	0.167	0.1688

Table S2. The contents of Li and Mn in spent LMO cathode.

Composition	Li (wt%)	Mn (wt%)
LMO	3.31	56.96

Table S3. The cost of raw materials.

Materials	Quantity (kg)	Unit price ($/kg)	Total cost ($)
$LiMn_2O_4$ batteries	1000	1.13	1130
Blue vitriol	266	0.3	79.8

Table S4. Expenditure and income of the pretreatment process.

Procedure	Expenditure item	Quantity	Unit price	Calculation	Total cost ($)
Discharging	Sodium chloride	53.5 kg	0.06 $/kg	/	3.21
	Deionized water	481.5 L	0.00053 L/kg	/	0.255
	Electricity	195 kW h	0.10 (kW h)$^{-1}$	/	19.5
Disassembling	Aluminum foil	40 kg	5.02 $/kg	/	-200.8
	Copper foil	25 kg	13.24 $/kg	/	-331
	Graphite	60 kg	0.24 $/kg	/	-14.4
	LMO	400 kg	Awaiting further processing		
PVDF removal	Electricity	147 kW h	0.10 (kW h)$^{-1}$	3.5*45/60+0.35*3=3.675 kw h (40times)	14.7

Table S5. Expenditure and income of the sulfation roasting-water leaching process.

Procedure	Expenditure item	Quantity	Unit price	Calculation	Total cost ($)
Roasting	Electricity	304 kW h	0.10 $(kW\ h)^{-1}$	6*70/60+0.6*1=7.6 kw h (40 times)	30.4
Water leaching	Deionized water	10460 L	0.00053 L/kg	/	5.5438
	CuO	80 kg	0.4876 $/kg	/	-78.016
	Mn_2O_3	320 kg	1.0727 $/kg	/	-686.528

Table S6. Expenditure and income of the precipitation process.

Compound	Quantity (kg)	Unit price ($/kg)	Total cost ($)
Sodium carbonate	106.0kg	0.181$/kg	19.186
Sodium sulfate	110.0kg	0.063$/kg	-6.93
Lithium carbonate	73.9kg	15.185$/kg	-1122.172

Table S7. Expenditure and income of the precipitation process.

Expenditure item	Quantity	Unit price	Total cost ($)
Labor	/	/	40
Equipment depreciation	/	/	370
Wastewater treatment	10941.5 L	0.20 $ $(m^3)^{-1}$	2.188

Table S8. Life cycle assessment calculation results.

Impact category	Global warming (GWP100a)	Abiotic depletion (fossil fuels)	Abiotic depletion	Human toxicity	Fresh water aquatic ecotox.
Unit	kg CO_2 eq	MJ	kg Sb eq	kg 1,4-DB eq	kg 1,4-DB eq
NaCl	1.44E+01	1.51E+02	4.43E-04	4.16E+01	1.91E+01
H_2O	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Al foil	-8.54E+02	-7.95E+03	-5.58E-04	-5.90E+02	-6.78E+02
Cu foil	-2.17E+02	-2.16E+03	-1.87E-01	-1.79E+04	-7.29E+03
Graphite	-3.60E+02	-5.42E+03	-1.16E-03	-2.27E+02	-1.16E+02
CuO	-4.87E+01	-5.24E+02	-4.69E-02	-4.49E+03	-1.82E+03
Mn_2O_3	-8.43E+01	-7.36E+02	-4.29E-04	-5.25E+01	-3.17E+01
Na_2CO_3	2.18E+02	2.66E+03	1.53E-03	1.86E+02	1.86E+02
Na_2SO_4	-9.58E+01	-1.07E+03	-2.70E-03	-1.62E+02	-8.17E+01
Li_2CO_3	-5.63E+02	-6.17E+03	-1.22E-02	-9.89E+02	-4.47E+02
Electricity	6.21E+02	5.62E+03	2.56E-03	4.31E+02	2.98E+02
Wastewater treatment	2.70E+00	2.23E+01	2.11E-05	6.85E+00	3.81E+00
Total	-1.36E+03	-1.55E+04	-2.46E-01	-2.37E+04	-9.96E+03

Table S9. The lithium recovery performance of spent NCM and LCO cathodes using blue vitriol-driven sulfation roasting method.

Cathode materials	Li recovery efficiency (%)	Li selective recovery ratio (%)
NCM	94.24	95.99
LCO	96.26	98.55

Text S1. Details of Characterization.

The Gibbs free energy changes of possible reactions and the phase evolution of Cu, Li, and Mn under varying temperatures and SO_2 partial pressures were computationally analyzed using HSC Chemistry 6.0 software. Thermogravimetric analysis (TG-DSC) of LMO, pure blue vitriol, and their mixtures was performed using the METTLER TOLEDO synchronous thermal analyzer (Switzerland) with a 10 ^{o}C /min heating rate from 25 ^{o}C to 1000 ^{o}C under air atmosphere; solution composition was quantified by ICP-MS (NexION 1000G, Singapore) to determine Li, Mn, and Cu mass fractions (wt.%); in-situ SO_2 release was monitored using an Afriso flue gas analyzer (China) under identical heating conditions (10 ^{o}C/min, 25-700 ^{o}C) with a 30-min holding time; crystalline phases were identified via X-ray diffraction (Rigaku MiniFlex600, Japan) at 7 ^{o}/min scanning rate over 10 ^{o}-80 ^{o}; chemical state evolution of Mn and S was tracked using XPS (Thermo Scientific K-ALPHA, USA); microstructural features and elemental distribution were characterized by SEM-EDS; and reaction mechanisms were further elucidated through density functional theory calculations performed in Materials Studio software.