Supporting Information

Microthermal catalytic aerogenesis of renewable biomass waste using cathode materials from spent lithium-ion batteries towards reversed regulated conversion and recycling of valuable metals

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Fig. S1. The pretreatment of spent LIBs for the obtaining the purified cathode materials of NCM.

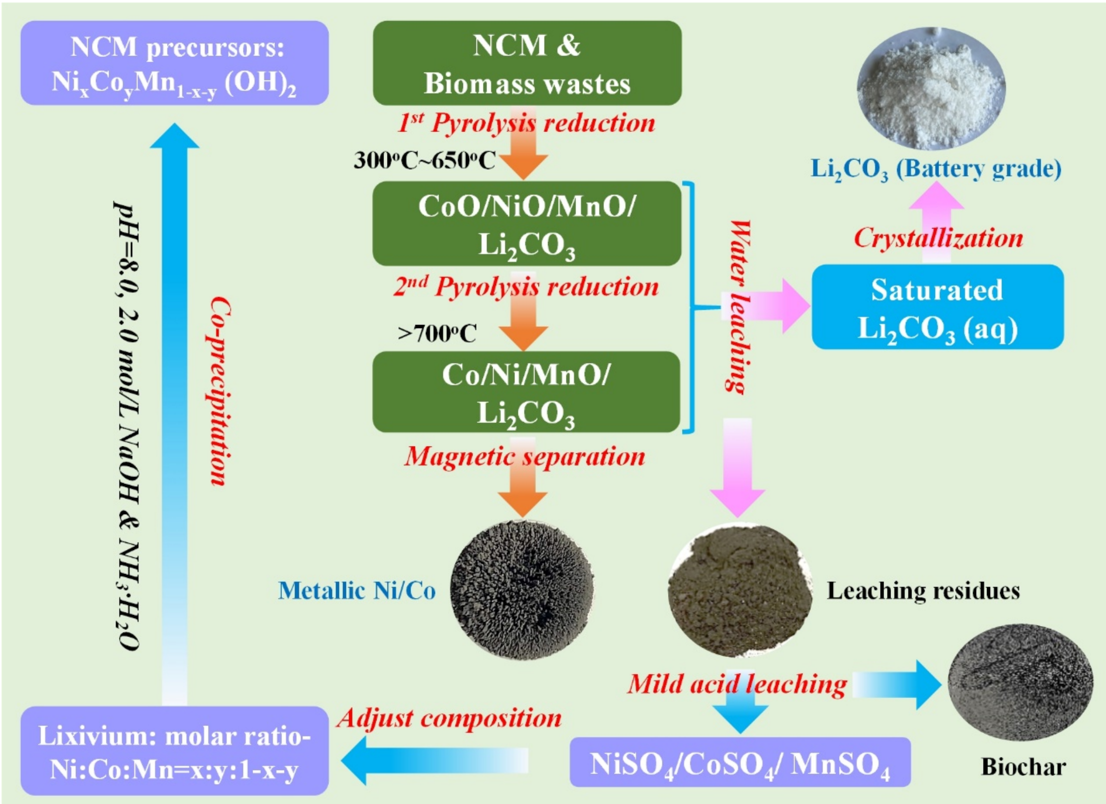

Fig. S2. Flow-chart for the recycling of valuable metals from spent LIBs.

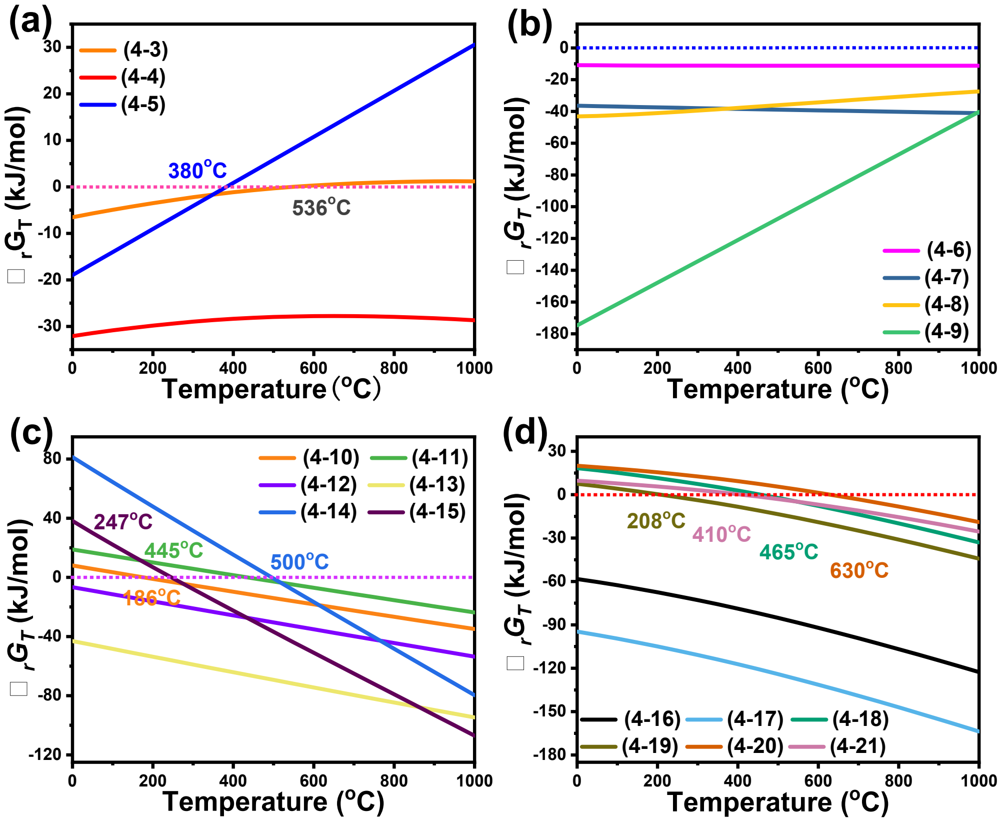

Fig. S3 Schematic diagram of relationship between the Gibbs free energy and reaction temperature during the reductive roasting process.

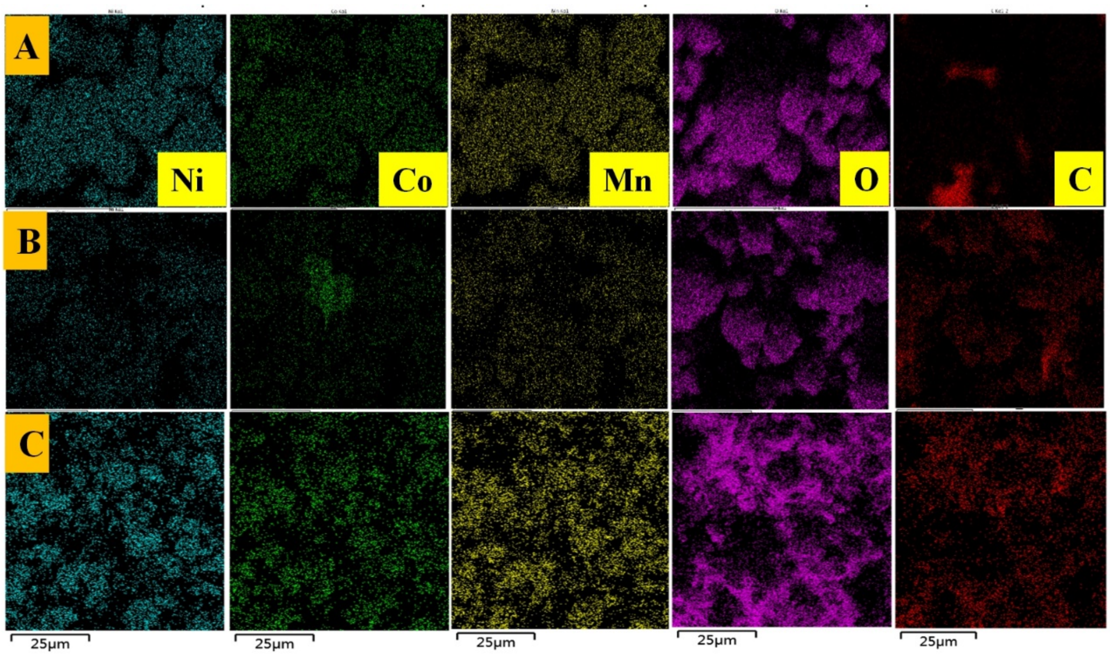

Fig. S4. EDS images for (A). cathode material and the roasted products of (B). at 500^{o}C and (C). 700°C under the condition of mass ratio of NCM:BMW=1:0.3.

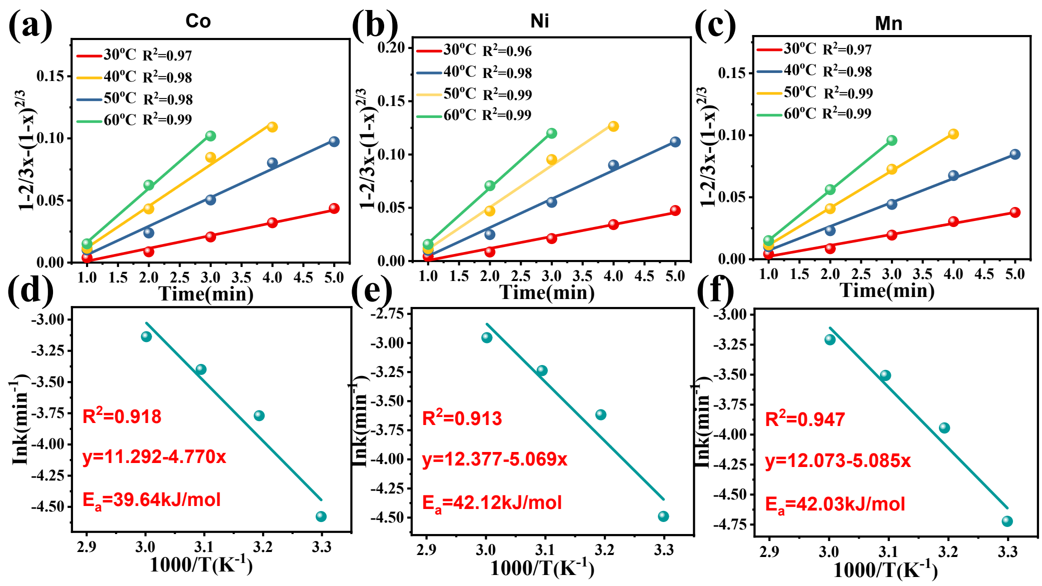

Fig. S5. Fitting results of "Ginstling-Brounshtein" at various leaching temperature for (a) cobalt, (b) nickel and (c) manganese; and arrhenius plots for leaching of (d) Co, (e)Ni and (f)Mn.

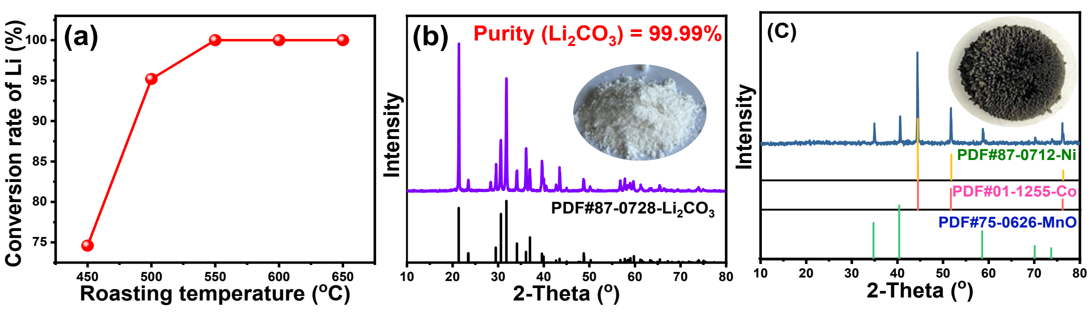

Fig. S6. XRD patterns of the recovered products (a-Li_2CO_3: 550°C) and b-Ni, Co and MnO: 700°C)

Fig. S7. Economic assessments of flow-chart for the recycling process of spent LIBs.

Table S1. Elementary composition of waste NCM and different samples.

Sample		Component rate (wt.%)							
		Ni	Co	Mn	Li	C	H	O	N
Spent NCM		30.61	12.54	17.32	1.821	/	/	/	/
1:0.3	450	26.64	10.89	14.58	1.306				
	500	25.47	10.42	14.33	0.999				
	550	27.88	11.43	15.88	1.206				
	600	26.41	10.82	14.88	1.262				
	650	28.56	11.72	16.20	1.405				
450	1:0.4	20.47	8.72	12.31	/				
	1:0.5	20.43	8.67	12.33	/				
	1:0.6	18.44	7.86	11.1	/				
Residue (Water leaching)	1:0.3 450	30.74	12.56	17.36	/				
Corn stalk		/	/	/	/	43.16	4.05	43.18	1.04

Table S2. The detailed information for the analytical instrument.

No.	Instrument	Types	Place of origin
1	ICP-OES	Intrepid II	American Thermofisher Company
2	XRD	D8 Advance	German Bruker Company
3	TG-DSC	TGA/DSC3+	Switzerland
4	XPS	AXIS SUPRA	Britain
5	GC	Agilent 7890B	America

Table S3. Fitting peaks of C1s XPS spectra of NCM powders roasted at different temperature.

Sample (°C)	Position1 (eV)	Area1 (wt%)	Position2 (eV)	Area2 (wt%)	Position3 (eV)	Area3 (wt%)	Position4 (eV)	Area4 (wt%)
NCM	284.8	69.65	285.8	16.29	288.99	14.06	-	-
500	284.8	56.99	286.3	16.28	289.7	23.09	293.1	3.64
550	284.8	51.46	286.0	22.48	289.8	22.07	293.0	3.98
600	284.8	58.75	285.9	10.68	289.7	28.54	292.9	2.03
650	284.8	38.54	285.5	30.6	289.7	26.35	293.0	4.52
700	284.8	53.98	286.4	15.44	289.6	23.27	292.6	7.32

Table S4. Fitting peaks of Ni2p XPS spectra of NCM powders roasted at different temperature.

Sample (^oC)	Position1 (eV)	Area1 (wt%)	Position2 (eV)	Area2 (wt%)	Position3 (eV)	Area3 (wt%)	Position4 (eV)	Area4 (wt%)
NCM	856.8	45.97	862.92	15.25	874.5	18.54	880.77	20.24
500	854.7	34.97	861.4	15.88	872.3	11.75	878.8	37.4
550	854.8	26.41	860.1	22.25	872.5	8.87	878.2	42.47
600	852.6	32.49	858.5	19.34	870.1	11.77	876.8	36.4
650	852.5	38.77	858.5	16.91	870.3	23.92	877.3	20.4
700	852.3	33.39	858.6	14.09	870.0	5.48	874.8	47.03

Table S5. Fitting peaks of Co2p XPS spectra of NCM powders roasted at different temperature.

Sample (ºC)	Position1 (eV)	Area1 (wt%)	Position2 (eV)	Area2 (wt%)	Position3 (eV)	Area3 (wt%)	Position4 (eV)	Area4 (wt%)
NCM	780.1	66.58	-	-	795.24	33.42	-	-
500	778.3	39.38	783.5	12	793.6	47.9	-	-
550	778.4	35.48	783.6	13.17	796.6	50.81	-	-
600	778.5	36.35	783.9	13.27	796.99	50.08	-	-
650	778.1	30.69	783.5	21.25	793.9	18.96	801.5	29.1
700	778.2	30.92	784.8	26.76	794.8	24.31	801.5	18.01

Table S6. Fitting peaks of Mn2p XPS spectra of NCM powders roasted at different temperature

Sample (^{o}C)	Position1 (eV)	Area1 (wt%)	Position2 (eV)	Area2 (wt%)	Position3 (eV)	Area3 (wt%)
NCM	642.3	79.83	-	-	653.8	20.17
500	642.4	61.99	-	-	652.2	39.01
550	642.4	77.39	-	-	653.6	22.61
600	640.3	34.55	643.0	36.23	652.7	34.55
650	640.2	48.55	643.3	22.76	652.4	28.69
700	640.2	55.43	644.3	24.65	652.4	19.93

Table S7 The possible chemical reactions and corresponding Gibbs free energy.

Reaction	**Caculation of** $\Delta_r G$	***Eq.***
$H_2(g)+NiO=Ni+H_2O$	$\Delta_r G$=-5.03+0.008T, kJ	(6)
$H_2(g)+MnO_2=MnO+H_2O$	$\Delta_r G$=-30.5+0.003T, kJ	(7)
$H_2(g)+CoO = Co+H_2O$	$\Delta_r G$=-18.97+0.05T, kJ	(8)
$CO(g)+NiO = Ni+CO_2(g)$	$\Delta_r G$=-11.03-2.65T, kJ	(9)
$CO(g)+MnO_2=MnO+CO_2(g)$	$\Delta_r G$=-36.5-0.005T, kJ	(10)
$CO(g)+CoO=Co+CO_2(g)$	$\Delta_r G$=-44.09+0.02T, kJ	(11)
$CO_2(g)+Li_2O = Li_2CO_3$	$\Delta_r G$=-174.74+0.13T, kJ	(12)
$C+NiO=Ni+CO(g)$	$\Delta_r G$=18.64-0.04T, kJ	(13)
$C+NiO=Ni+CO_2(g)$	$\Delta_r G$=7.60-0.04T, kJ	(14)
$C+MnO_2=MnO+CO(g)$	$\Delta_r G$=-6.83-0.05T, kJ	(15)
$C+MnO_2=MnO+CO_2(g)$	$\Delta_r G$=-43.34-0.05T, kJ	(16)
$C+CoO = Co+CO(g)$	$\Delta_r G$=80.11-0.16T, kJ	(17)
$C+2CoO = 2Co+CO_2(g)$	$\Delta_r G$=36.02-0.14T, kJ	(18)
$CH_4+3MnO_2=3MnO+CO(g)+2H_2O$	$\Delta_r G$=-54.64-0.07T, kJ	(19)
$CH_4+4MnO_2=4MnO+CO_2(g)+2H_2O$	$\Delta_r G$=-91.14-0.07T, kJ	(20)
$CH_4+3NiO=3Ni+CO(g)+2H_2O$	$\Delta_r G$=21.77-0.05T, kJ	(21)
$CH_4+4NiO=4Ni+CO_2(g)+2H_2O$	$\Delta_r G$=10.74-0.05T, kJ	(22)
$CH_4+3CoO=3Co+CO(g)+2H_2O$	$\Delta_r G = 23.28 - 0.04T$, kJ	(23)

$CH_4+4CoO=4Co+CO_2(g)+2H_2O$	$\Delta_r G$ =12.74 − 0.04T, kJ	(24)

Table S8. The detailed cost of energy consumption during metal recycling.

Unit operation	**Energy cost (kW.h)**	**Expenditure ($)**
Pyrolysis roasting	90	-7.03
Water leaching	33	-2.58
Crystallization	22	-1.72
Drying	2.6	-0.2
Acid leaching	3.3	-0.25
Magnetic separation	0.74	-0.06
Total	151.64	-11.84

Table S9. The detailed cost of chemical reagents and materials during metal recycling.

Substance	**Price ($/kg)**	**Weight (kg)**	**Expenditure ($)**
BMW	0.04	0.5	-0.02
H_2SO_4	0.09	0.06	-0.01
Total	-	-	-0.03

Table S10. Economic benefits from recycling different components of 1 kg spent LIBs.

Substance	Price ($/kg)	Weight (kg)	Economic benefit ($)
Li_2CO_3	30	0.33	9.9
Ni	23.47		
Co	78	0.60	19.38
MnO	14		
$MnSO_4$	1.61		
$CoSO_4$	14.5	1	6.32
$NiSO_4$	5.56		
Total	-	-	35.6

Table S11. Related waste control and disposal of 1 kg spent LIBs.

Waste type	Disposal ($/t)	Weight	Cost ($)
Waste solid	147.1×10^{-3}	0.15 kg	-0.02
Waste water	0.412×10^{-3}	20 L (~20 kg)	-0.01
Waste gas	92.88×10^{-3}	10.69 kg	-0.99
Total	-	-	-1.02

Table S12. A brief comparison of different reduction roasting processes.

Methodology	Sample	Equipment	Condition	Product	Ref.
Carbothermal reduction	NCM	Microwave reactor	18 wt.% Carbon; 650°C; 1500 W	MnO	1
	LCO	Vacuum reactor	Graphite: LCO=1:5; 700°C; 45min	Li_2CO_3; Co/CoO	2
	*NCM	Tube furnace	Graphite; 700°C; 90 min	Co/CoO; Ni/NiO; Mn/Mn_3O_4; Li_2O/Li_2CO_3	3
Thermite reduction	NCM	Tube furnace	Aluminum; 520°C; 60min	$LiAlO_2$; NiO/CoO/MnO	4
	LCO	Tube furnace	Aluminum; 600°C; 60 min	Li_2O/$LiAlO_2$; CoO	5
Sulfating roasting	LCO	Muffle furnace	$NaHSO_4 \cdot H_2O$: LCO=1.4:1; 600°C; 30 min	Co_3O_4	6
Biomass reduction	NCM	Microwave reactor	24 wt.% Macadamia Shells; 500°C-750°C; 25 min	Li_2CO_3; Ni/Co/MnO	7
	MnO_2 Ore	Tube furnace	Bamboo scraps: Ore=10:1; 400°C; 10 min	MnO	8
	NCM	Tube furnace	Corn stalk: NCM =0.3:1; 450°C-700°C; 15 min	Li_2CO_3; CoO/NiO/MnO; Co/Ni/MnO.	**This study**

Note: LCO- $LiCoO_2$; NCM- $LiNi_xCo_yMn_zO_2$; *NCM- a mixture of $LiCoO_2$, $LiMnO_2$ and $LiNiO_2$.

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