Supporting Information

Recycling cathodes from spent lithium-ion batteries based on the selective extraction of lithium

Xing Shen[1], Bo Li[1], Xin Hu[1], Chuan-Fu Sun[4], Yong-Sheng Hu[2], Chao Yang[1], Huizhou Liu[1*] and Junmei Zhao[1,3*]

[1] CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190

[2]Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Mat erials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institu te of Physics, Chinese Academy of Sciences, Beijing 100190, China.

[3]Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, China

[4]CAS Key Laboratory of Design and Assembly of Functional Nanostructures and Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China

Corresponding authors

[*]Huizhou Liu. Email address: hzliu@ipe.ac.cn

[*]Junmei Zhao. Email address: jmzhao@ipe.ac.cn

No. 1 Zhongguancunbeierjie road, Haidian District, Beijing, P.R.China 100190

Number of pages: 18

Number of figures: 2

Number of tables: 13

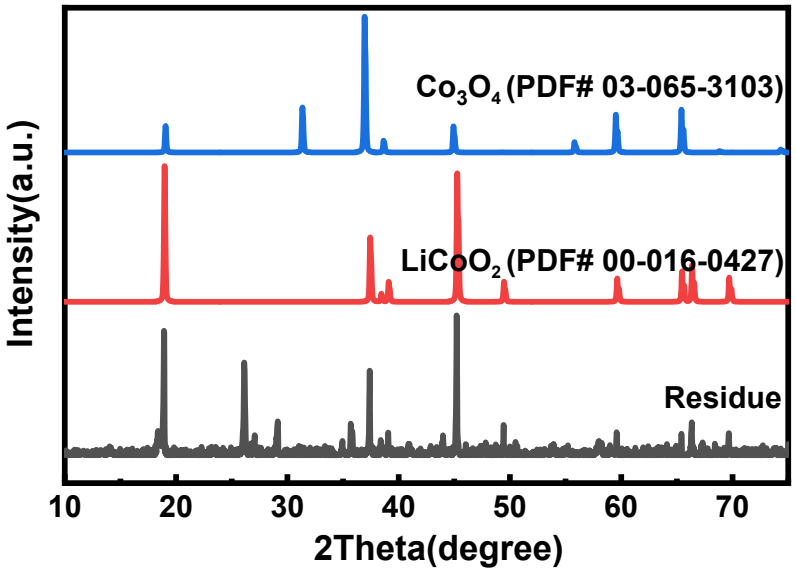

Figure S1 The XRD pattern of residue after heat treatment at 160 °C for 12 h without water atmosphere

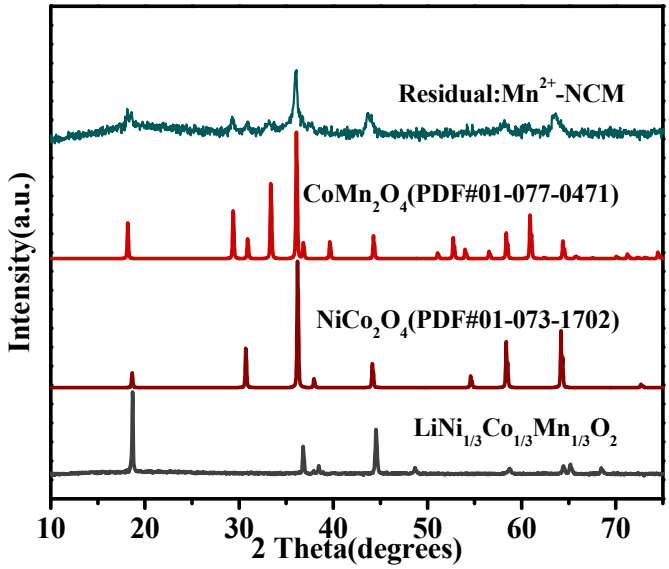

Figure S2 The XRD patterns of the solid product for the reaction between Mn^{2+} and NCM

Table S1 Elemental contents of the commercial pristine cathode materials ($LiCoO_2$, $LiMn_2O_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$)

Elemental concentration	Li (mg/g)	Ni (mg/g)	Co (mg/g)	Mn (mg/g)
$LiCoO_2$	71.0		555.9	
$LiMn_2O_4$	44.75			805.13
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	72.43	184.8	192.0	180.8

Table S2 The consumed Co^{2+} and the generated Li^{+} in the filtrate at different reaction time

Time (h)	2	4	6	8	12
Li^{+} (mol/L)	0.1144	0.5750	0. 7990	0.9391	1.023
reduced Co^{2+} (mol/L)	0.0669	0.3017	0.4167	0.4588	0.5132
Li^{+}/Co^{2+}	1.71	1.91	1.92	2.05	1.99

Table S3 Gibbs free energies of the reaction between LCO and Co^{2+} at different temperature calculated by HSC Chemistry 6.0.

Temperature (℃)	120	130	140	150	160
$\Delta_r G$ (kJ/mol)	-109.54	-111.35	-113.19	-115.06	-116.95

Table S4 Thermodynamic data of relevant chemical compounds used for the calculation.

Compound	ΔH_{fus}^{θ} ($kJ \cdot mol^{-1}$)	S^{θ} ($J \cdot mol^{-1} \cdot k^{-1}$)	$C_p = A + B \times 10^{-3} T + C \times 10^{5} T^{-2} + D \times 10^{-6} T^{2}$			
			A	B	C	D
$LiCoO_2$	-679.4	52.17	321.45	-758.99	-79.01	722.03
Co^{2+}	-58.158	-112.968	-2010.2	8802.5	306.8	-11008.5
Co_3O_4	-910.02	114.31	131.65	66.02	-24.80	0.00
Li^{+}	-278.45	12.24	-728.31	3273.22	146.42	-3941.74

Table S5 The consumed Mn^{2+} and the generated Li^{+} in the filtrate at different reaction time

Time(h)	1	2	4	6	8	12
Li^{+} (mol/L)	0.1788	0.5250	0.5439	0.5882	0.5914	0.5990
reduced Mn^{2+} (mol/L)	0.1157	0.2683	0.2889	0.2963	0.3048	0.3083
Li^{+}/Mn^{2+}	1.54	1.96	1.88	1.99	1.94	1.94

Table S6 Li^+ extraction efficiency (Li%), the residual rate (M%) of Ni^{2+}, Co^{2+} and Mn^{2+} for the decomposition of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the solution of Mn^{2+}, Co^{2+} and Ni^{2+} at 160 ^oC for 8 h with a S/L ratio of 100 g/L

Leaching agent	Ni^{2+}	Co^{2+}	Mn^{2+}
Li%	27.48	86.08	100.40
Ni%	57.20	—	—
Co%	0.21	10.74	—
Mn%	—	—	0.20

'—' demonstrates that it is below the detection limit.

Table S7 Elemental contents (wt%) of spent NCM-cathode scrap

Real powder	Li	Ni	Co	Mn	Al
NCM-cathode scrap	5.59%	23.4%	10.6%	10.9%	8.04%

Table S8 Extraction mass balances for the extraction of lithium from NCM-cathode scrap by $MnSO_4$

Content	Mass (g)	Li (g)	Ni (g)	Co (g)	Mn (g)	Al (g)
replacement ion	——	——	——	——	10.28	——
LCO-cathode scrap	50	2.896	11.68	5.323	5.455	4.021
filtrate	——	2.816	——	——	——	——
extraction/residual rates in the filtrate	——	97.2%	——	——	——	——
leaching slag	66	0.1915	11.43	5.16	15.18	3.88
residual rates in the slag	——	6.61%	97.86%	96.94%	96.47%	96.49%
mass balance	——	103.81%	97.86%	96.94%	96.47%	96.49%

Reaction conditions：NCM-cathode scrap 50 g, 200℃, 24 h, S/L=100.

Table S9 The pH variations for the reaction system of NCM-cathode scrap and Mn^{2+} before and after the reaction

Real powder	content	pH
NCM-cathode scrap	NCM-cathode scrap in deionized water	10.83
	$MnSO_4$ solution	6.76
	NCM-cathode scrap in $MnSO_4$ solution	6.81
	filtrate	9.90

Table S10 Elemental compositions (wt%) of the LCO-cathode scraps

Real powder	Li	Ni	Co	Mn	Al
LCO-cathode scraps	6.61%	——	57.4%	——	0.44%

‘—‘ demonstrates that it is below the detection limit.

Table S11 Extraction mass balances for the extraction of lithium from LCO-cathode scraps by $CoSO_4$

Content	Mass (g)	Li^+ (mg)	Co^{2+} (mg)	Al^{3+} (mg)
extractant	——	——	1022.75	——
LCO-cathode scraps	4.0	264.24	2296.16	17.6
filtrate	——	253.25	0.442	——
extraction/residual rates in the filtrate	——	95.84%	——	——
leaching slag	4.536	26.17	3201.08	18.22
residual rates in the slag	_____	6.9%	96.45%	103.5%
mass balance	_____	102.74%	96.46%	103.5%

Reaction conditions：LCO-cathode scraps 4 g, 200℃, 24 h, S/L=100.

Table S12 pH varies for the decomposition of LCO-cathode scraps in the solution of $CoSO_4$ before and after the reaction

Real powder	content	pH
LCO-cathode scraps	LCO-cathode scraps in deionized water	10.35
	$CoSO_4$ solution	3.71
	LCO-cathode scraps in $CoSO_4$ solution	6.74
	Filtrate after the reaction	7.33

Table S13 The electrochemical performance comparison between R-LCO and other typical regenerated $LiCoO_2$ reported.

Capacity (mAh g^{-1})	Current density	Capacity retention	Voltage range (V)	Rate performance mAh g^{-1}	reference
153	0.2C		2.5-4.3		Ref.[1]
150.3	0.1C	93.2%（100cycles）	3-4.3		Ref.[2]
148.2	1C	91.2%（100cycles）	3-4.3	2C=141.9; 5C=130.3	Ref.[3]
138.6	0.2C	86%（200cycles））	3-4.2	2C=111	Ref.[4]
144.5	0.2C	92.5%（200cycles）	2.75-4.25	5C=115.3 2C=127.5	Ref.[5]
132.5	20mA g^{-1}	90.1%（100cycles）	3-4.2		Ref.[6]
136	0.2C	No decay（200cycles）	3-4.3		Ref.[7]
132.1	0.2C	96.7%（50cycls）	2.8-4.2		Ref.[8]
131.2	1C	84.5%（100cycles）	2.8-4.3	5C=110	Ref.[9]
137.9	1C	94.6% (100cycles)	2.5-4.2	2C=137.6 5C=134.9 10C=129.3 15C=119.3	This work
144.9			2.5-4.3		
162.5			2.5-4.4		

References

1. Li, J.; Zhao, R.; He, X.; Liu, H., Preparation of $LiCoO_2$ Cathode Materials from Spent Lithium-ion Batteries. *Ionics* **2008,** *15* (1), 111-113, DOI 10.1016/S0378-7753(02)00037-X.

2. Chen, S.; He, T.; Lu, Y.; Su, Y.; Tian, J.; Li, N.; Chen, G.; Bao, L.; Wu, F., Renovation of $LiCoO_2$ with Outstanding Cycling Stability by Thermal Treatment with Li_2CO_3 from Spent Li-ion Batteries. *J. Energy Storage* **2016,** *8*, 262-273, DOI 10.1016/j.est.2016.10.008.

3. Shi, Y.; Chen, G.; Chen, Z., Effective Regeneration of $LiCoO_2$ from Spent Lithium-ion Batteries: a Direct Approach towards High-performance Active Particles. *Green Chem.* **2018,** *20* (4), 851-862, DOI 10.1039/C7GC02831H.

4. Wang, B.; Lin, X.-Y.; Tang, Y.; Wang, Q.; Leung, M. K. H.; Lu, X.-Y., Recycling $LiCoO_2$ with methanesulfonic acid for regeneration of lithium-ion battery electrode materials. *J. Power Sources* **2019,** *436*, 226828, DOI 10.1016/j.jpowsour.2019.226828.

5. Yang, J.; Wang, W.; Yang, H.; Wang, D., One-pot compositional and structural regeneration of degraded LiCoO2 for directly reusing it as a high-performance lithium-ion battery cathode. *Green Chem.* **2020,** *22* (19), 6489-6496, DOI 10.1039/D0GC02662J.

6. Gao, Y.; Li, Y.; Li, J.; Xie, H.; Chen, Y., Direct Recovery of $LiCoO_2$ from the Recycled Lithium-ion Batteries via Structure Restoration. *J. Alloy Compd.* **2020,** *845*, 156234, DOI 10.1016/j.jallcom.2020.156234.

7. Zhang, L.; Xu, Z.; He, Z., Electrochemical Relithiation for Direct Regeneration of LiCoO2 Materials from Spent Lithium-Ion Battery Electrodes. *ACS Sustain. Chem. Eng.* **2020,** *8* (31), 11596-11605, DOI 10.1021/acssuschemeng.0c02854.

8. Zhao, S.; Zhang, W.; Li, G.; Zhu, H.; Huang, J.; He, W., Ultrasonic Renovation Mechanism of Spent LCO Batteries: A Mild Condition for Cathode Materials Recycling. *Resour. Conserv. Recy.* **2020,** 162, DOI 10.1016/j.resconrec.2020.105019.

9. Zhou, S.; Zhang, Y.; Meng, Q.; Dong, P.; Fei, Z.; Li, Q., Recycling of $LiCoO_2$ Cathode Material from Spent Lithium Ion Batteries by Ultrasonic Enhanced Leaching and One-step Regeneration. *J. Environ. Manage.* **2021,** *277*, 111426, DOI 10.1016/j.jenvman.2020.111426.