Supporting information

Direct regeneration method of spent $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials via surface lithium residues

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Table S1. Atomic percentage of Li, Ni, Co and Mn in S-NCM, R-NCM800, R-NCM850 and R-NCM900 respectively.

Samples	Li	Ni	Co	Mn
S-NCM	7.53	17.9	21	17
R-NCM800	7.81	17.9	21.5	18.2
R-NCM850	7.81	18.7	22	18
R-NCM900	7.13	18.8	22.5	18.9

Table S2. Moral ratio of Li, Ni, Co and Mn in S-NCM, R-NCM800, R-NCM850 and R-NCM900, respectively.

Samples	Li	Ni	Co	Mn	Formula
S-NCM	1.085	0.304	0.356	0.309	$Li_{1.085}Ni_{0.304}Co_{0.356}Mn_{0.309}O_{1.999}$
R-NCM800	1.125	0.304	0.364	0.331	$Li_{1.125}Ni_{0.304}Co_{0.364}Mn_{0.331}O_{2.075}$
R-NCM850	1.125	0.318	0.373	0.327	$Li_{1.125}Ni_{0.318}Co_{0.373}Mn_{0.327}O_{2.094}$
R-NCM900	1.027	0.32	0.381	0.344	$Li_{1.027}Ni_{0.320}Co_{0.381}Mn_{0.344}O_{2.093}$

The Li content in S-NCM measured by ICP-OES was 1.08 mole, which is mainly attributed to the over-discharge process to 2.0V before the dismantlement of spent LIBs. Based on the voltage variations, that over-discharge process was ascribed into first stage which voltage would drop rapidly. And it is due to over-discharge which causes Li^+ to be deintercalated from the anode and inserted into the cathode.[1] Consequently, the Li content in S-NCM materials would shows quite increasement after that pre-treatment owing to the insertion of Li^+. While the components of S-NCM also contains some lithium-containing impurities besides active layered-structure materials, including LiF and lithium carbonate after long-term cycles,[2] which can be confirmed with FT-IR and TG-DSC tests. The lithium residues on the surface is partly attributed to the side-reaction between the positive electrode material and the electrolyte. According to previous study, it has been proven that soluble lithium salts such as Li_2CO_3 and LiOH can act as Li source to supply Li deficiency in material lattice to enhance the integrity of layered structure of NCM materials.[3, 4] Besides, lithium contained compounds would decompose during the high-temperature calcination, which could react with the NiO to remove those impurities with poor conductivity. With that recrystallization of layered NCM structures under O_2 atmosphere to avoid oxygen loss, it would be favorable for transport kinetics for both lithium ions and electrons, improving its electrochemical performance. Based on this fact, here we proved that these surface lithium residues could be recycled to regenerate spent NCM materials without other consumption.

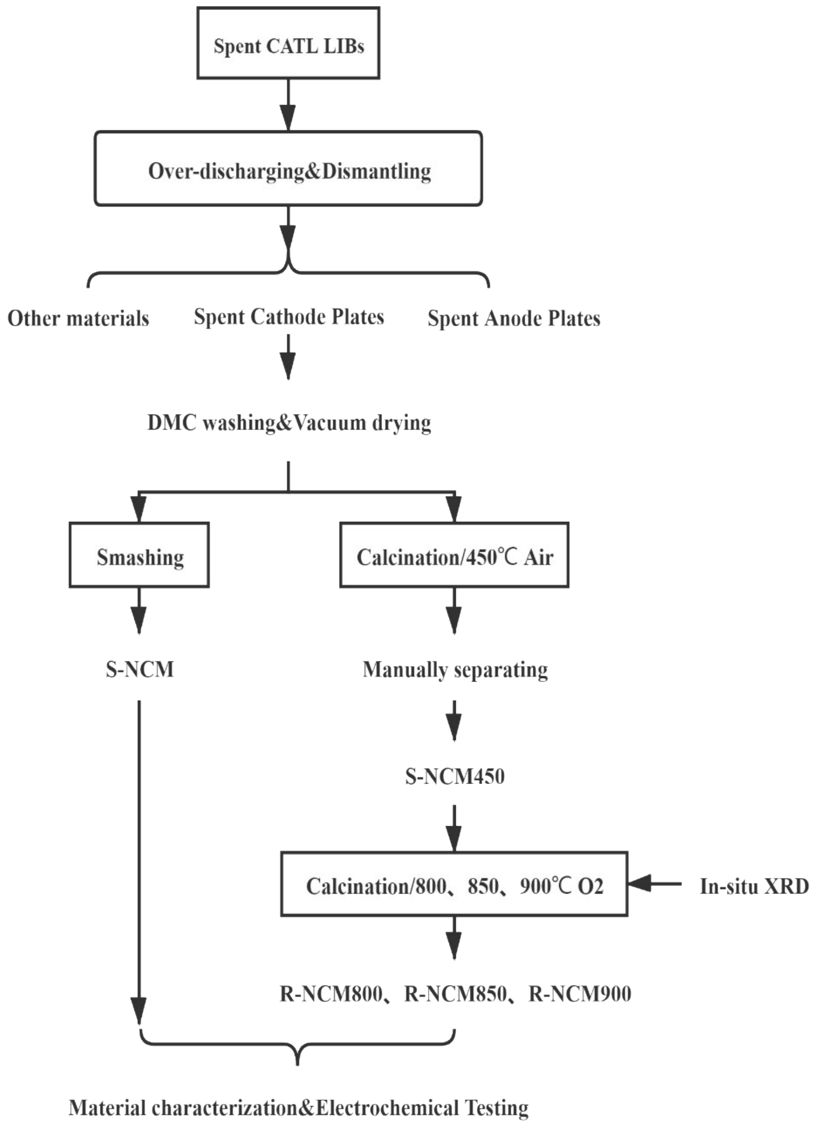

Figure S1. Schematic diagram for experimental process.

Figure S2. Spent prismatic lithium-ion batteries.

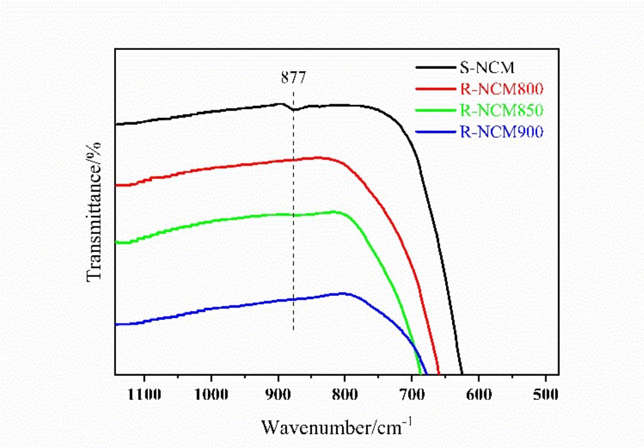

Figure S3. Enlarged FT-IR images of spent and regenerated NCM materials.

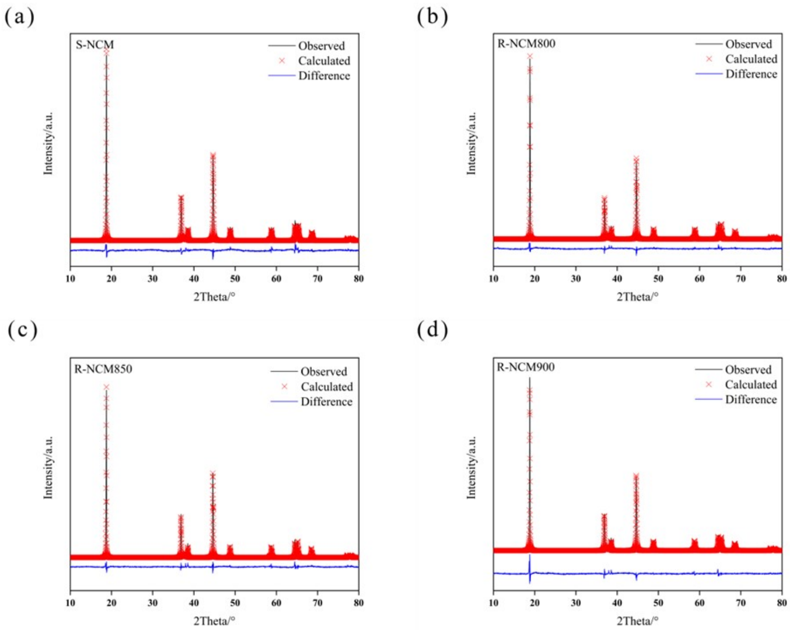

Figure S4. Rietveld refinement of ex-situ XRD patterns of (a)S-NCM, (b)R-NCM800, (c)R-NCM850 and (d) R-NCM900.

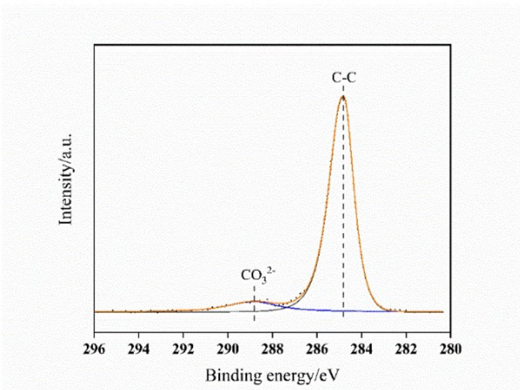

Figure S5. Enlarged C1s XPS spectrum of S-NCM450.

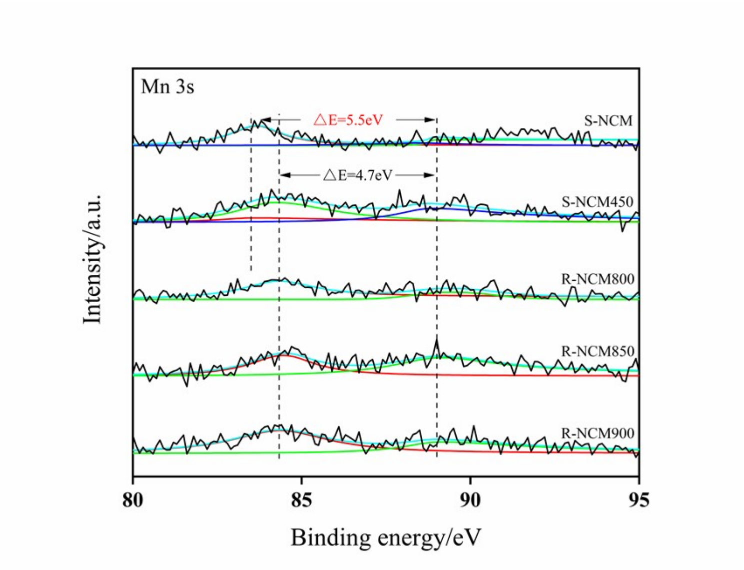

Figure S6. XPS spectra of Mn 3s of S-NCM and R-NCM.

As shown in Fig.S6, all of these samples show two splitting distinct peaks at 89.0 eV and 84.3 eV, which corresponds to Mn^{4+}. Besides, there also shows a distinct peak at 83.5 eV attributed to Mn^{3+}.[5] The XPS spectra of Mn 3s is consistent with the results of Mn 2p.

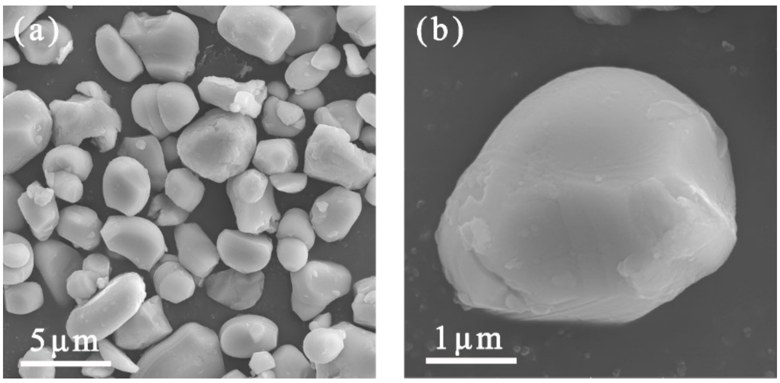

Figure S7. SEM images of S-NCM450 at different resolution.

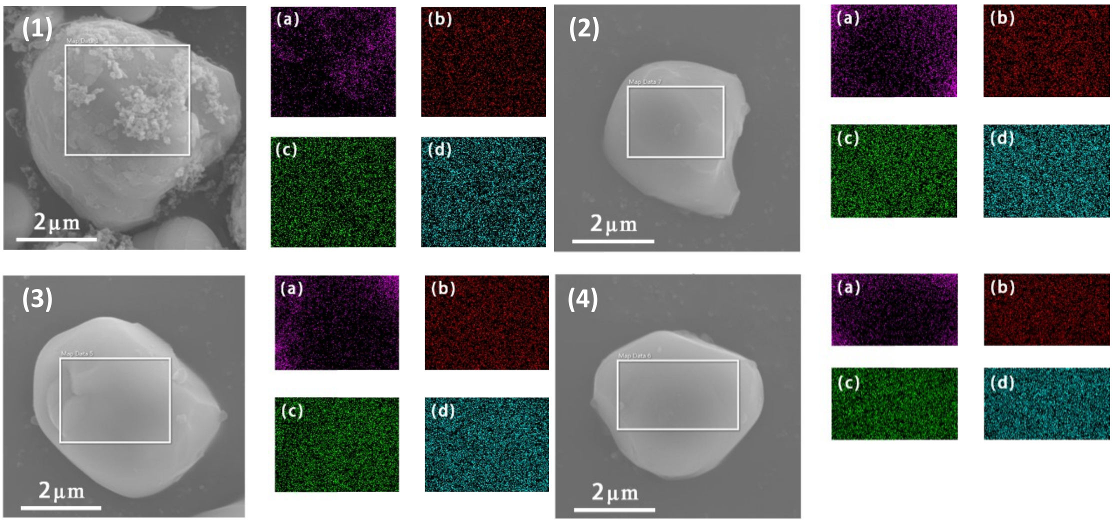

Figure S8. EDX elemental mappings of (1)S-NCM, (2)R-NCM800, (3)R-NCM850 and (4)R-NCM900 corresponding to (a) C, (b) Ni, (c) Co, (d) Mn, respectively.

Table S3. Comparison of the electrochemical performances of R-NCM850 with other reported regenerated materials with additional lithium compounds.

Rate	**R-NCM850 2.8-4.3V**	NCM (ref6, Li_2CO_3) 2.7-4.3V	NCM (ref7, CH_3COOLi) 2.8-4.3V	NCM (ref8, Li_2CO_3) 2.7-4.3V
0.2	**156.2**	148.8	151.6	--
0.5	**145.6**	141.6	145.7	150
1	**139.2**	132.9	138.3	145
5	**115.6**	--	120.6	100

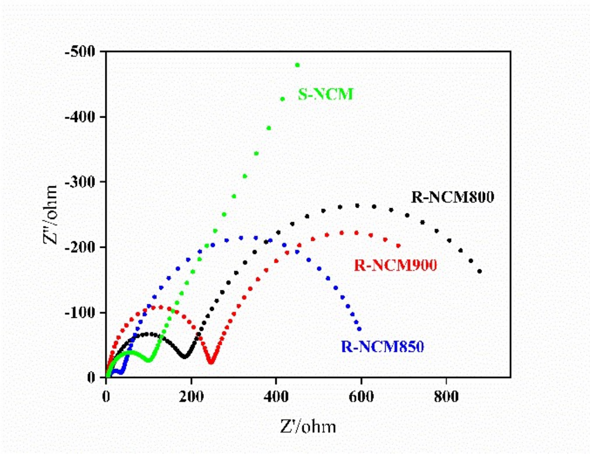

Figure S9. Enlarged Nyquist plots of S-NCM, R-NCM800, R-NCM850 and R-NCM900 at high frequency area.

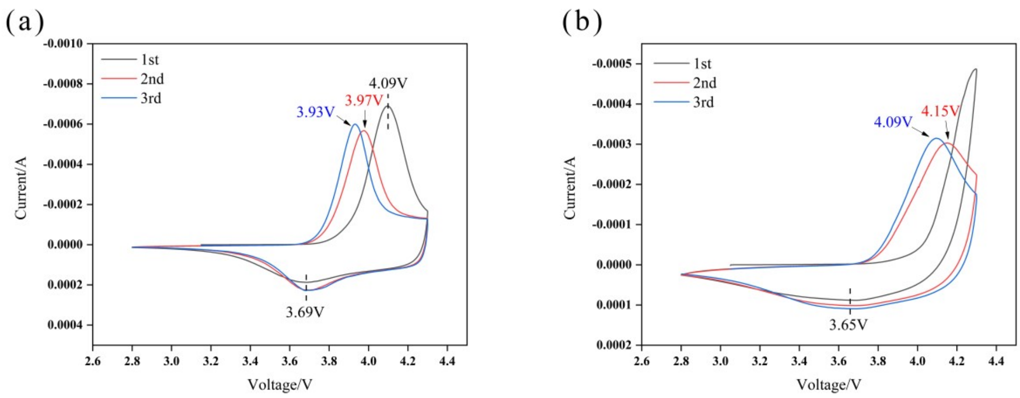

Figure S10. Cyclic voltammograms of (a)R-NCM800 and (b)R-NCM900 during the first 3 cycles.

Table S4. Material consumption to direct regenerate or synthesize 1kg NCM111 cathode materials

	Direct regeneration	Synthesized[ref]
$NiSO_4$/kg	--	0.5348
$CoSO_4$/kg	--	0.5356
$MnSO_4$/kg	--	0.5218
Spent cathode materials/kg	1.2	--
Li_2CO_3/kg	--	0.4021
H_2O/kg	--	5.1835
NaOH/kg	--	0.6220
$NH_3 \cdot H_2O$/kg	--	0.5449
DMC/kg	0.3(reused)	--

References

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