Supporting information

A vapor thermal approach to selectively recycling spent lithium-ion batteries

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Tab. S1 Main components of different types of spent cathode powders.

Content	Li (wt%)	Co (wt%)	Ni (wt%)	Mn (wt%)
Commerce $LiCoO_2$	6.69	57.12		
Commerce $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622)	7.17	12.03	36.38	11.35
Commerce $LiMn_2O_4$	3.83			60.77

Tab. S2 $I_{(003)}/I_{(104)}$ peak ratios of $LiCoO_2$ at different temperatures (XC-0.6N-2h-3H, X = 190-230 °C).

Temperature	1	2	3	4	5	6	7	8	9	10
190 °C		4.09		3.9		3.51		3.3		3.1
200 °C		3.1		2.2						
210 °C	1.89	1.85								
220 °C	2.26	1.88								
230 °C	2.54	1.9								

Tab. S3 Detailed information of the added ammonium salts for treating different types of cathode materials (1 g of $LiCoO_2$, NCM622, $LiMn_2O_4$).

Ammonium salts	M (g/mol)	$LiCoO_2$	NCM622	$LiMn_2O_4$
NH_4Cl	53.49		0.6g	
$(NH_4)_2SO_4$	132.14		0.7341	
$(NH4)_2SO_3 \cdot H_2O$	134.14		0.745	
$(NH_4)_2CO_3$	96.09		1.2338	
NH_4HSO_4	115.12		1.279	
NH_4HCO_3	79.05		0.8784	
$(NH4)_3PO_4 \cdot 3H_2O$	203.09		0.7341	
$(NH_4)_2HPO_4$	132.06		0.7339	
$NH_4H_2PO_4$	115.03		1.2781	
NH_4F	37.0		0.4115	
NH_4HCO_2	63		0.7007	
NH_4OAc	77.08		0.8564	
$C_6H_5O_7(NH_4)_3$	243.22		0.9008	
$NH_3 \cdot H_2O$	0.91 g cm^{-3}		1.556 mL	

Tab. S4 The optimized reaction condition for treating different types of cathode materials with ammonium salts.

Cathode material	Temperature (°C)	Time (hour)	H_2O (mL)
$LiCoO_2$ (1g)	220 °C	4	3
NCM622 (1g)	220 °C	4	3
$LiMn_2O_4$ (1g)	230 °C	4	3

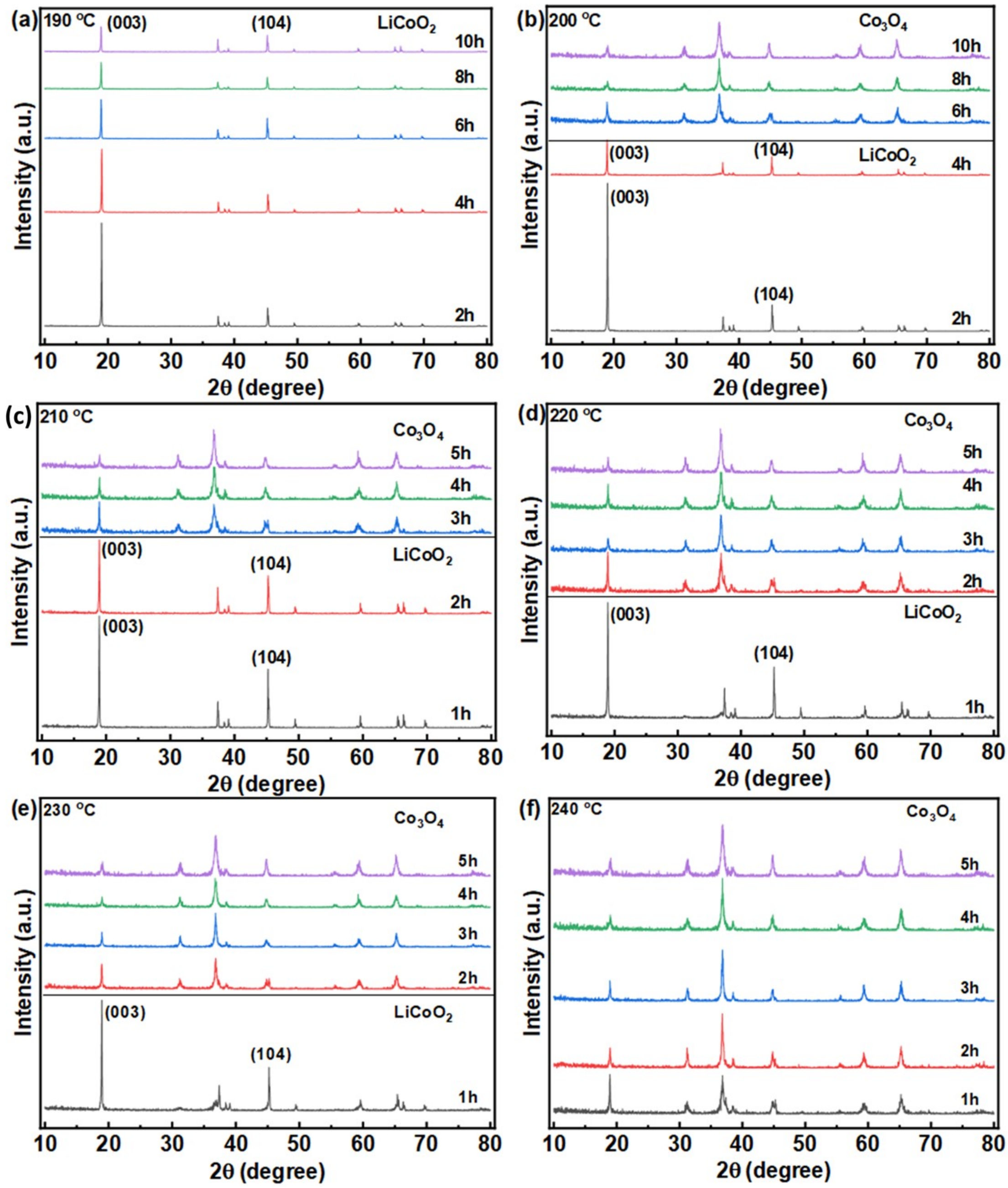

Fig. S1 XRD patterns of the products after the reaction between 1 g of $LiCoO_2$ and NH_4Cl at different times for (a) 190C-0.6N-Xh-3H, (b) 200C-0.6N-Xh-3H, (c) 210C-0.6N-Xh-3H, (d) 220C-0.6N-Xh-3H, (e) 230C-0.6N-Xh-3H, and (f) 240C-0.6N-Xh-3H (X refers different reaction time).

The reaction equations of $LiCoO_2$ and different types of ammonium salts by vapor thermal reduction

$NH_4Cl + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 8LiOH + LiCl + 1/2N_2$ (1)

$1/2(NH_4)_2SO_4 + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 8LiOH + 1/2Li_2SO_4 + 1/2N_2$ (2)

$1/2(NH_4)_2CO_3 + 9LiCoO_2 + 2.5H_2O = 3Co_3O_4 + 9LiOH + 1/2CO_2 + 1/2N_2$ (3)

$NH_4HSO_4 + 9LiCoO_2 + H_2O = 3Co_3O_4 + 7LiOH + Li_2SO_4 + 1/2N_2$ (4)

$NH_4HCO_3 + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 9LiOH + CO_2 + 1/2N_2$ (5)

$1/2(NH_4)_2SO_3 + 12LiCoO_2 + 3.5H_2O = 4Co_3O_4 + 11LiOH + 1/2Li_2SO_4 + 1/2N_2$ (6)

$1/3(NH_4)_3PO_4 + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 8LiOH + 1/3Li_3PO_4 + 1/2N_2$ (7)

$1/2(NH_4)_2HPO_4 + 9LiCoO_2 + 1.5H_2O = 3Co_3O_4 + 7.5LiOH + 1/2Li_3PO_4 + 1/2N_2$ (8)

$NH_4H_2PO_4 + 9LiCoO_2 = 3Co_3O_4 + 6LiOH + Li_3PO_4 + 1/2N_2$ (9)

$NH_4F + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 8LiOH + LiF + 1/2N_2$ (10)

$NH_4HCO_2 + 14LiCoO_2 + 4.5H_2O = 4.5Co_3O_4 + 1/2CoCO_3 + 14LiOH + 1/2CO_2 + 1/2N_2$ (11)

$NH_4OAc + 33LiCoO_2 + 13H_2O = 11Co_3O_4 + 33LiOH + 2CO_2 + 1/2N_2$ (12)

$1/3(NH_4)_3C_6H_5O_7 + 26LiCoO_2 + 61/6H_2O = 17/2Co_3O_4 + 1/2CoCO_3 + 26LiOH + 3/2CO_2 + 1/2N_2$ (13)

$NH_4NO_3 + 9LiCoO_2 + 2H_2O = 3Co_3O_4 + 8LiOH + LiNO_3 + 1/2N_2$ (14)

$NH_3 \cdot H_2O + 9LiCoO_2 = 3Co_3O_4 + 5LiOH + 2Li_2O + 1/2N_2$ (15)

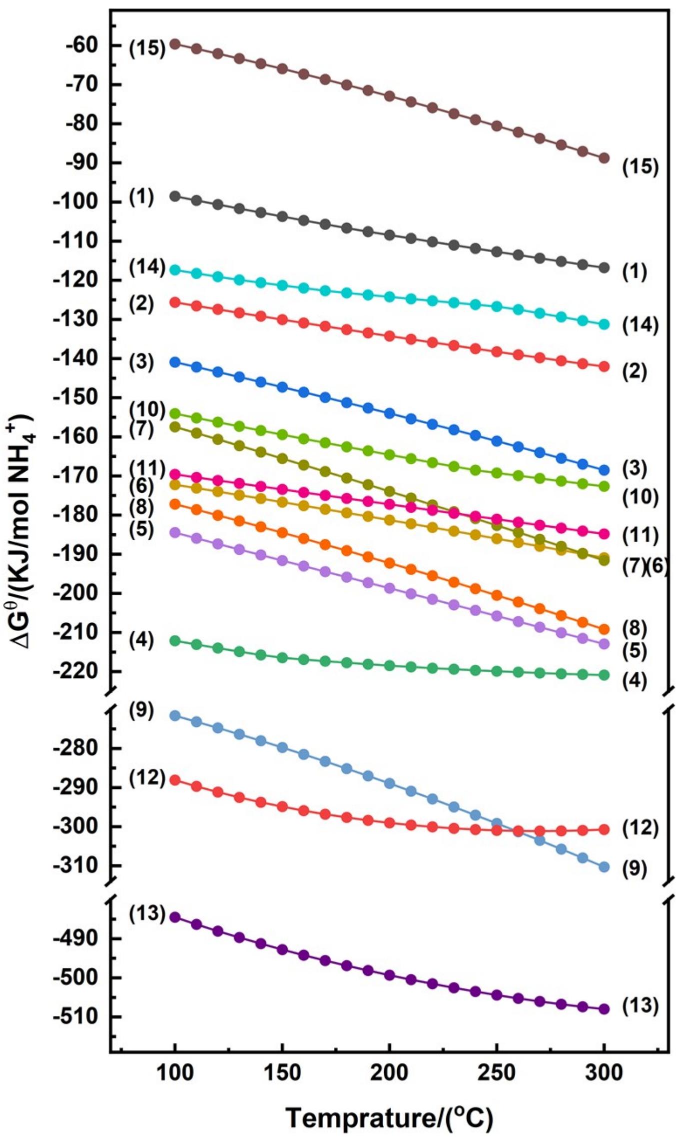

Fig. S2 Profiles of Gibbs free energy as a function of temperature of typical reactions between $LiCoO_2$ and different kinds of ammonium salts.

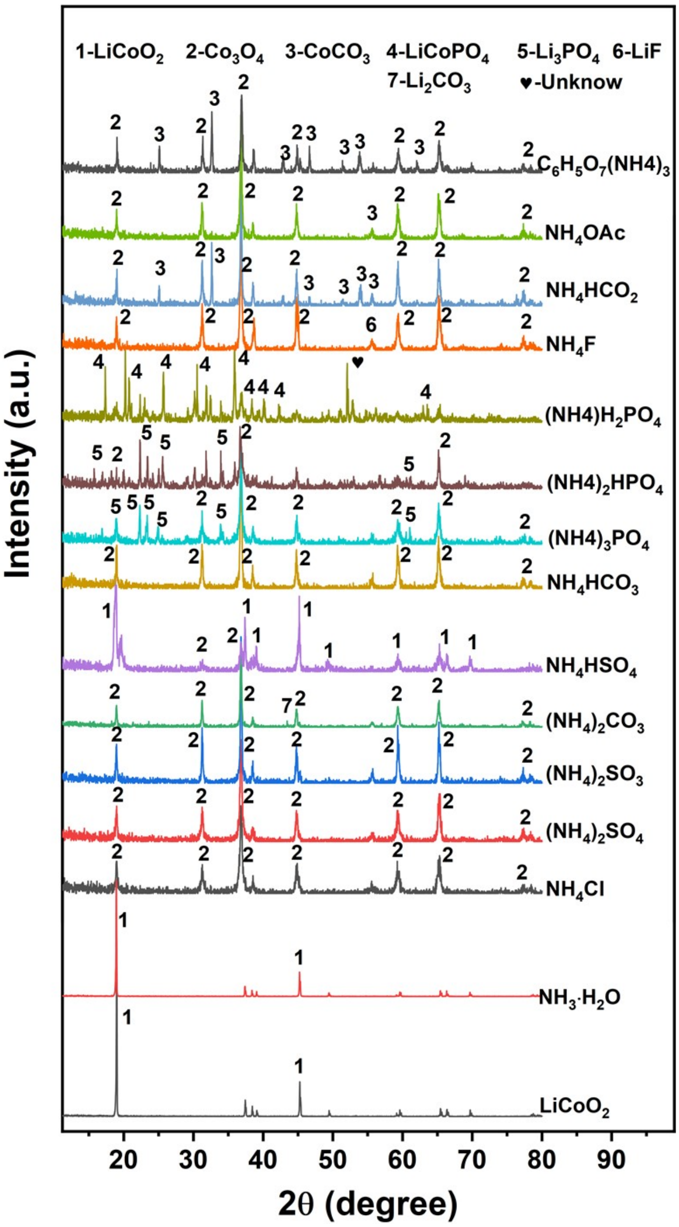

Fig. S3 XRD patterns of pure $LiCoO_2$, and the products obtained from $LiCoO_2$ and ammonium salts after vapor thermal reduction (220C-XN-4h-3H, X denotes different kinds of ammonium salts, the usage of ammonium salts was shown in **Tab. S3**)

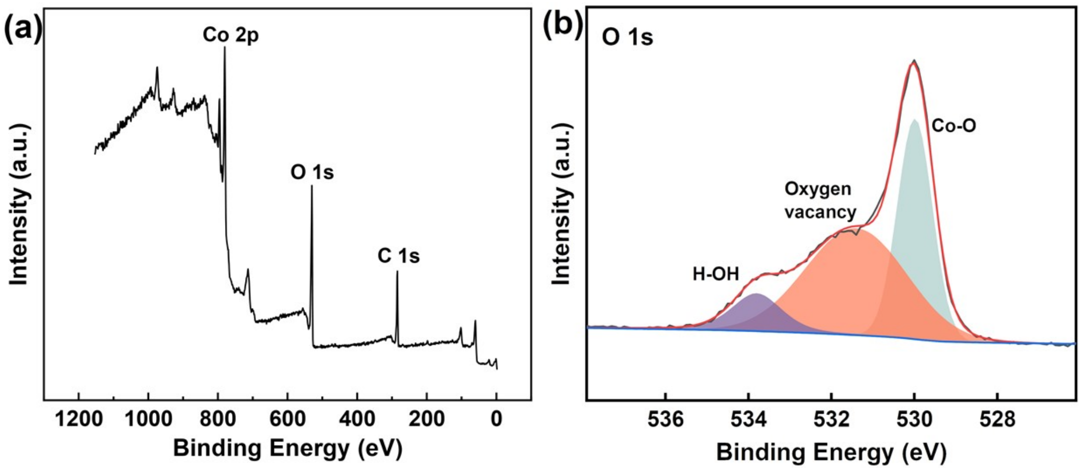

Fig. S4 XPS spectra of the product obtained at 220C-0.6N-4h-3H (1g of $LiCoO_2$) (a) a survey of the products, (b) O 1s.

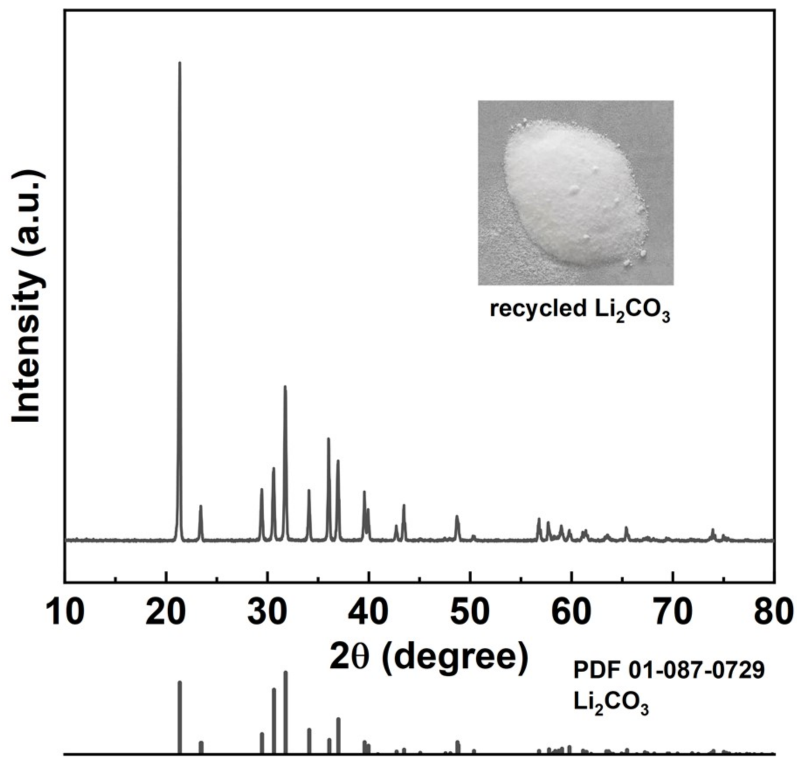

Fig. S5 Pure Li_2CO_3 obtained by adding 2 M Na_2CO_3 solution into leachate ($LiCoO_2$ treated by NH_4Cl, 220C-0.6N-4h-3H).

Reaction equations of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) and ammonium salts by vapor thermal reduction.

$NH_4Cl + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + LiCl + 1/2N_2$ (16)

$1/2(NH_4)_2SO_4 + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + 1/2Li_2SO_4 + 1/2N_2$ (17)

$1/2(NH_4)_2CO_3(ia) + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 17/14H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 45/7LiOH + 1/2CO_2 + 1/2N_2$ (18)

$NH_4HSO_4 + 45/7 LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 31/7LiOH +Li_2SO_4 + 1/2N_2 + 2/7H_2O$ (19)

$NH4HCO_3 + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 45/7LiOH + CO_2 + 1/2N_2$ (20)

$1/2(NH_4)_2SO_3 + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + 1/2Li_2SO_4 + 1/2N_2$ (21)

$1/3(NH_4)_3PO_4 + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + 1/3Li_3PO_4 + 1/2N_2$ (22)

$1/2(NH4)_2HPO_4 + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 3/14H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 69/14LiOH + 1/2Li_3PO_4 + 1/2N_2$ (23)

$NH_4H_2PO_4 + 45/7 LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 24/7LiOH + Li_3PO_4 + 1/2N_2 + 9/7H_2O$ (24)

$$NH_4F + 45/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + LiF + 1/2N_2 \quad (25)$$

$$NH_4HCO_2 + 10\ LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/2H_2O = 6NiO + 1/2CoCO_3 + 1/2Co_3O_4 + 2MnO_2 + 10LiOH + 1/2CO_2 + 1/2N_2 \quad (26)$$

$$NH_4OAc + 165/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 58/7H_2O = 99/7NiO + 11/7Co_3O_4 + 33/7MnO_2 + 165/7LiOH + 2CO_2 + 1/2N_2 \quad (27)$$

$$1/3(NH4)_3C_6H_5O_7 + 120/7LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 241/42H_2O = 72/7NiO + 3/2CoCO_3 + 9/14Co_3O_4 + 24/7MnO_2 + 120/7LiOH + 1/2CO_2 + 1/2N_2 \quad (28)$$

$$NH_4NO_3 + 45/7\ LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 + 5/7H_2O = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 38/7LiOH + LiNO_3 + 1/2N_2 \quad (29)$$

$$NH_3{\cdot}H_2O(l) + 45/7\ LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 = 27/7NiO + 3/7Co_3O_4 + 9/7MnO_2 + 35/7LiOH + 5/7Li_2O + 1/2N_2(g) \quad (30)$$

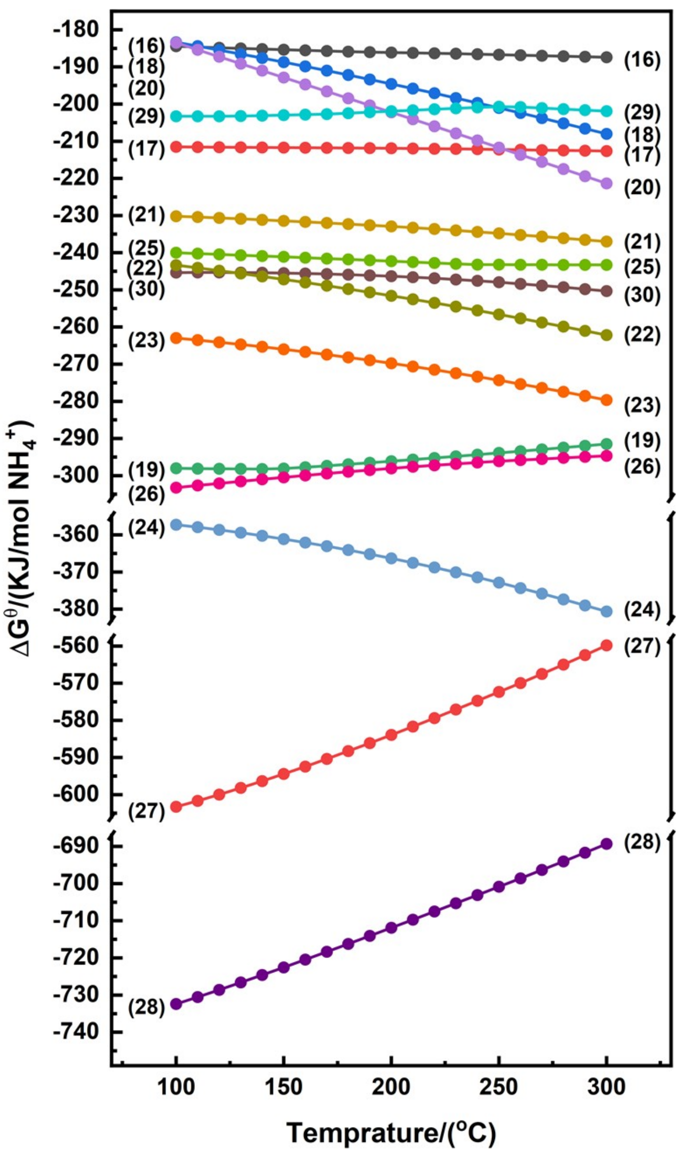

Fig. S6 Profiles of Gibbs free energy as a function of temperature of the reactions between NCM622 and ammonium salts.

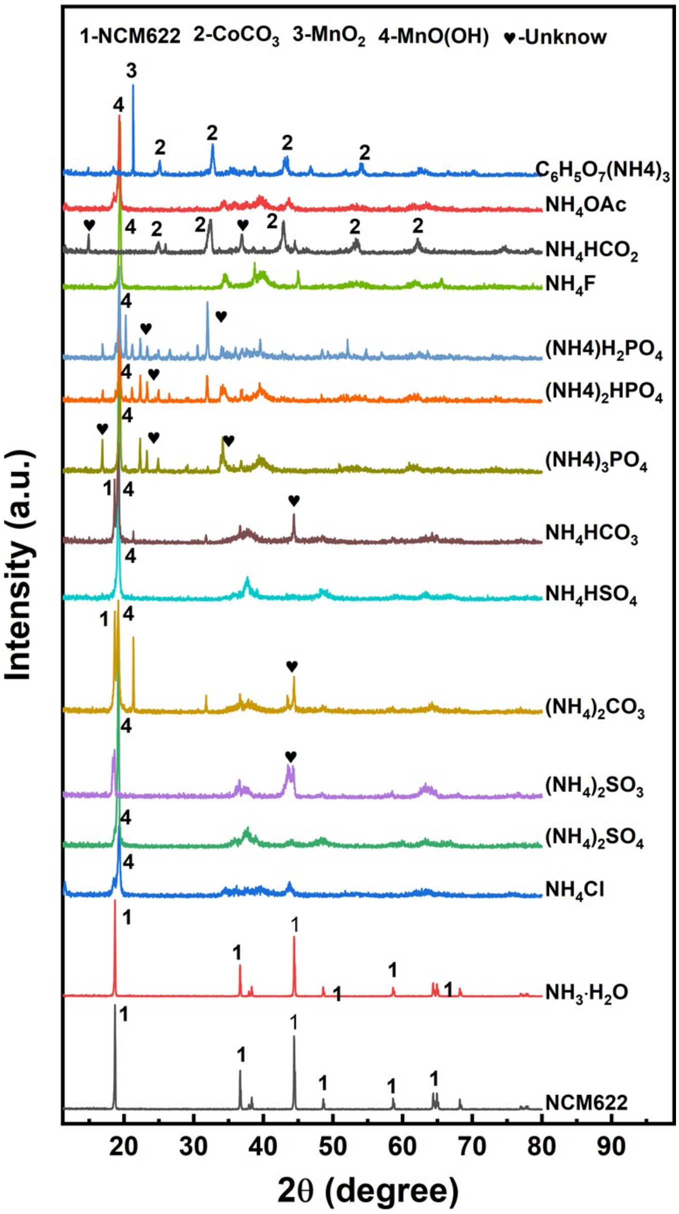

Fig. S7 XRD patterns of pure NCM622 and the products obtained from NCM622 and ammonium salts after vapor thermal reduction (220C-XN-4h-3H, X denotes different kinds of ammonium salts, the usage of ammonium salts was shown in **Tab. S3**).

The NCM622 cathode has the same layered crystal structure with $LiCoO_2$, so the volume of water, reaction time, temperature, and the amount of ammonium salts were kept consistent with $LiCoO_2$. However, $LiMn_2O_4$ has a spinel structure instead. In order to determine its optimum reaction temperature, the leaching experiment under different temperatures was designed (**Fig. S8)**. The volume of water, reaction time, and the usage of ammonium salt were kept consistent with $LiCoO_2$. As shown in **Fig. S8**, the leaching efficiency of Li reached 99.8% at 230 °C, while the leaching rate of Mn was only 0.01%. Hence, the optimal reaction temperature for $LiMn_2O_4$ was 230 °C. The usage of ammonium salts was listed in **Tab. S3**. The reaction equations of NCM622 and $LiMn_2O_4$ are **equations 16-30** and **equations 31-45**, respectively. In addition, thermodynamic calculations are shown in **Fig. S6** and **Fig. S9**.

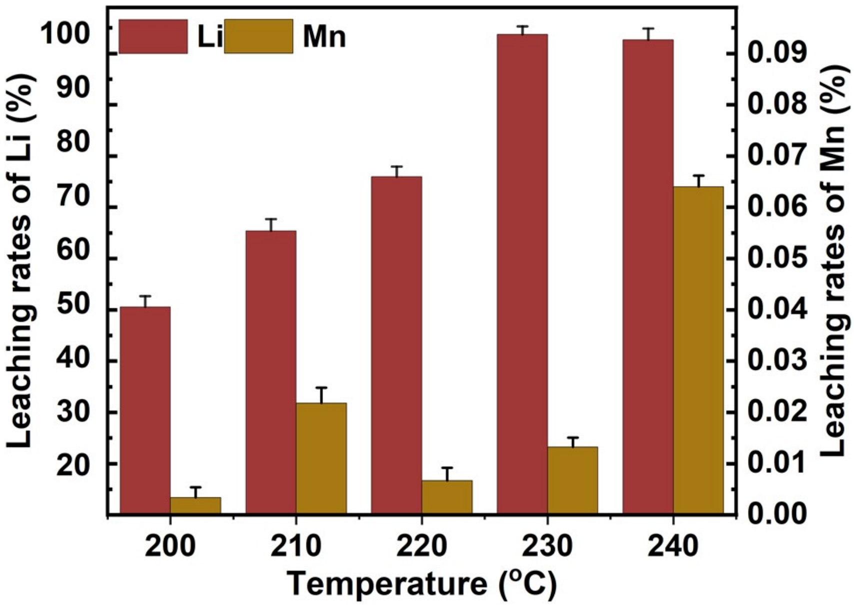

Fig. S8 Leaching rates of Li and Mn of $LiMn_2O_4$ under different temperatures (XC-0.73N-4h-3H, X = 200-240 °C).

The reaction equations of $LiMn_2O_4$ and ammonium salts by vapor thermal reduction.

$NH_4Cl + 6LiMn_2O_4 + 1/2H_2O(g) = 11/4Mn_3O_4 + 21/4MnO_2 + 5LiOH + LiCl + 12/N_2$ (31)

$1/2(NH_4)_2SO_4 + 6LiMn_2O_4 + 1/2H_2O(g) = 9/4Mn_3O_4 + 21/4MnO_2 + 5LiOH + 1/2Li_2SO_4 + 1/2N_2$ (32)

$1/2(NH_4)_2CO_3(ia) + 5LiMn_2O_4 + 1/2H_2O(g) = 2Mn_3O_4 + 4MnO_2 + 5LiOH + 1/2CO_2(g) + 1/2N_2$ (33)

$NH_4HSO_4 + 8LiMn_2O_4 + 1/2H_2O(g) = 11/4Mn_3O_4 + 31/4MnO_2 + 6LiOH + Li_2SO_4 + 1/2N_2$ (34)

$NH_4HCO_3 + 6LiMn_2O_4 + 1/2H_2O(g) = 9/4Mn_3O_4 + 21/4MnO_2 + 6LiOH + CO_2(g) + 1/2N_2$ (35)

$1/2(NH_4)_2SO_3 + 6LiMn_2O_4 + 1/2H_2O(g) = 5/2Mn_3O_4 + 9/2MnO_2 + 5LiOH + 1/2Li_2SO_4 + N_2$ (36)

$1/3(NH_4)_3PO_4 + 6LiMn_2O_4 + 5/6H_2O(g) = 9/4Mn_3O_4 + 21/4MnO_2 + 5LiOH + 1/3Li_3PO_4 + 1/2N_2$ (37)

$(NH_4)_2HPO_4 + 14LiMn_2O_4 + H_2O(g) = 5Mn_3O_4 + 13MnO_2 + 11LiOH + Li_3PO_4 + N_2$ (38)

$NH_4H_2PO_4 + 10LiMn_2O_4 + 1/2H_2O(g) = 13/4Mn_3O_4 + 41/4MnO_2 + 7LiOH + Li_3PO_4 + 1/2N_2$ (39)

$NH_4F + 6LiMn_2O_4 + 12/H_2O(g) = 9/4Mn_3O_4 + 21/4MnO_2 + 5LiOH + LiF + 1/2N_2$ (40)

$NH_4HCO_2 + 6LiMn_2O_4 + 1/2H_2O(g) = 9/4Mn_3O_4 + 17/4MnO_2 + 6LiOH + MnCO_3 + 1/2N_2$ (41)

$NH_4OAc + 8LiMn_2O_4 + 1/2H_2O(g) = 15/4Mn_3O_4 + 11/4MnO_2 + 8LiOH + 2MnCO_3 + 1/2N_2$ (42)

$1/3(NH_4)_3C_6H_5O_7 + 20/3LiMn_2O_4 + 1/2H_2O(g) = 35/12Mn_3O_4 + 31/12MnO_2 + 20/3LiOH + 2MnCO_3 + 1/2N_2$ (43)

$NH_4NO_3 + 6LiMn_2O_4 + 2/3H_2O(g) = 11/6Mn_3O_4 + 13/2MnO_2 + 16/3LiOH + 2/3LiNO_3 + 2/3N_2$ (44)

$NH_3{\cdot}H_2O + 4 LiMn_2O_4 = 7/4Mn_3O_4 + 11/4MnO_2 + 4LiOH + 1/2N_2 + 1/2H_2O(g)$ (45)

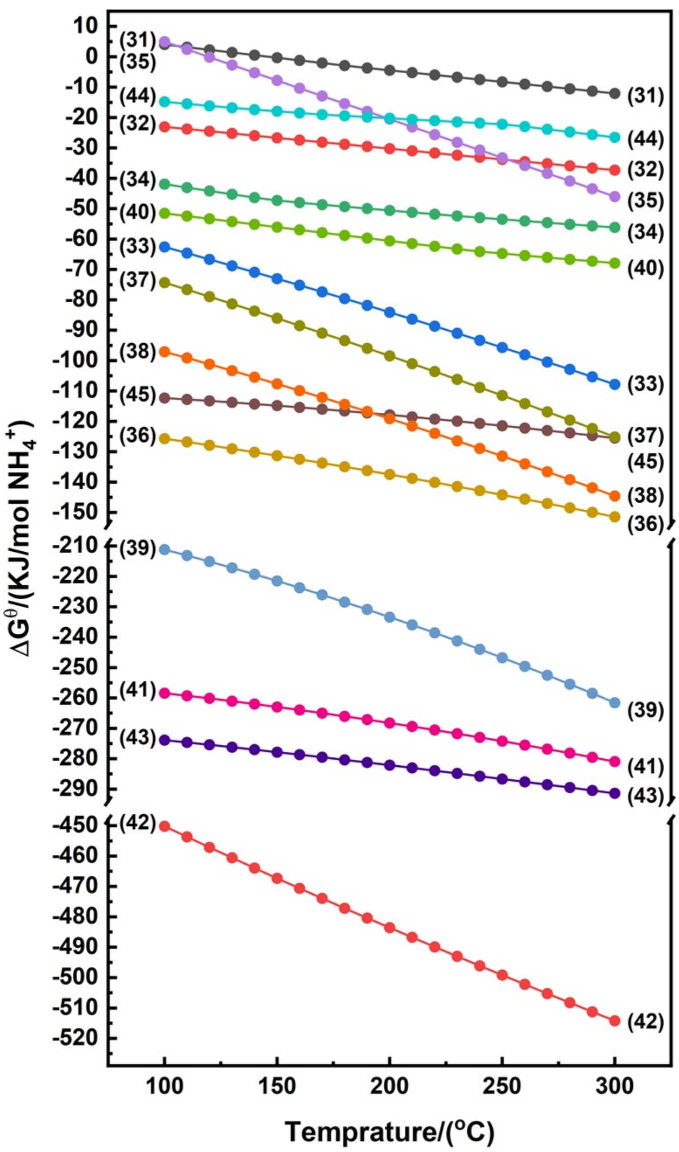

Fig. S9 Profiles of Gibbs free energy as a function of temperature of the reactions between $LiMn_2O_4$ and ammonium salts.

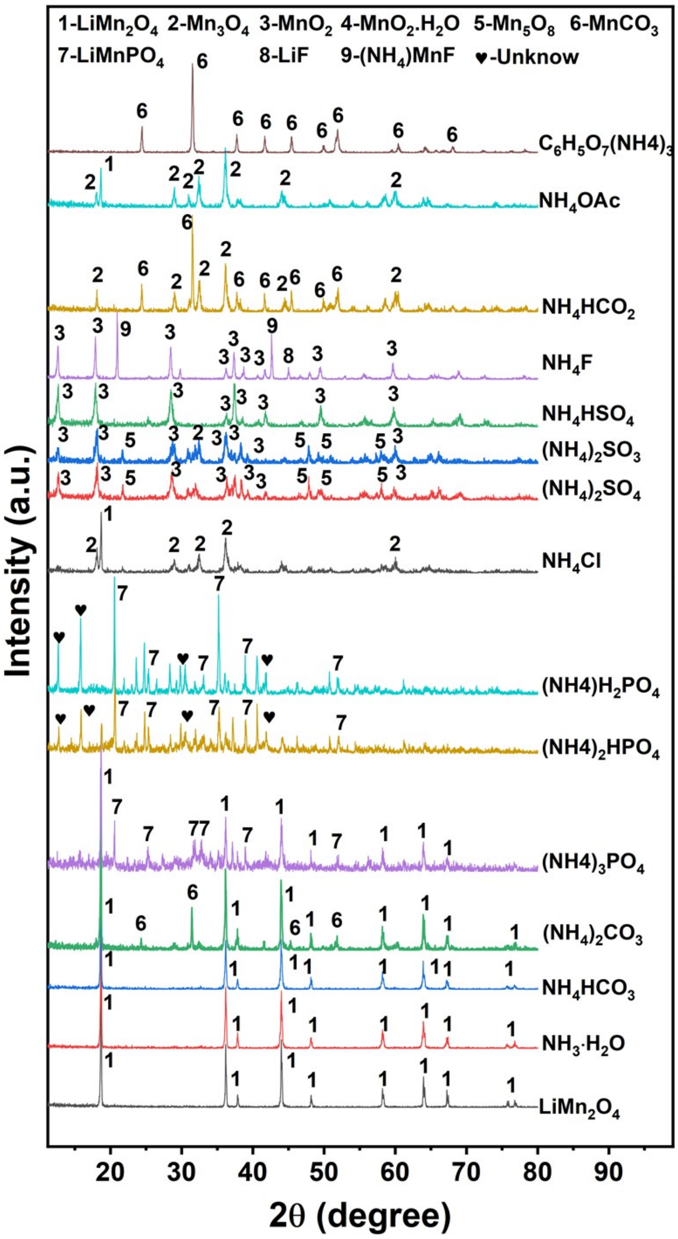

Fig. S10 XRD patterns of pure $LiMn_2O_4$, and the products obtained from $LiMn_2O_4$ and ammonium salts after vapor thermal reduction, (230C-XN-4h-3H, X denotes different kinds of ammonium salts, the usage of ammonium salts was shown in **Tab. S3**).

Tab. S5 Leaching rates of Li, Ni, Co, and Mn for treat typical cathode materials (1 g of $LiCoO_2$, NCM622, and $LiMn_2O_4$) using different types of ammonium salts.

Ammonium Salt	$LiCoO_2$		NCM622				$LiMn_2O_4$	
	Li/ (%)	Co/ (%)	Li/ (%)	Ni/ (%)	Co/ (%)	Mn/ (%)	Li/ (%)	Mn/ (%)
NH_4Cl	98.7	0.021	89.01	6.16	0.41	0.041	89.2	0.001
$(NH_4)_2SO_4$	90.74	0.053	99.17	0.24	0.03	0.001	99.8	0.07
$(NH_4)_2SO_3{\cdot}H_2O$	99.78	0.038	98.98	0.04	0.02	0.02	99.7	0.027
$(NH_4)_2CO_3$	37.3	0.107	50.69	0.07	0.05	0.001	50.65	0.033
NH_4HSO_4	61.69	20.13	99.71	16.85	1.66	0.008	99.6	86.43
NH_4HCO_3	47.45	0.122	58.13	0.07	0.05	0.001	0.02	0.001
$(NH_4)_3PO_4{\cdot}3H_2O$	1.58	0.046	1.49	0.43	0.18	0	4.87	0.206
$(NH_4)_2HPO_4$	0.36	0.011	1.05	0.17	0.19	0	5.05	0.066
$NH_4H_2PO_4$	2.44	0.053	9.56	0.07	0.01	0.024	53.89	0.183
NH_4F	19.74	0.014	16.46	0.42	0.01	0	99.4	20.67
NH_4HCO_2	89.68	0.616	81.6	6.02	0.65	0.002	99.8	0.005
NH_4OAc	98.49	0.077	93.19	2.13	0.67	0.003	93.94	0.008

$C_6H_5O_7(NH_4)_3$	81.2	0.74	74.24	12.42	2.17	0.004	99.4	0.003
$NH_3 \cdot H_2O$	0.96	0.004	2.16	0.001	0	0	13.7	0.094

Tab. S6 Chemical components of products obtained from cathode materials (1 g of $LiCoO_2$, NCM622, and $LiMn_2O_4$) which were treated with different types of ammonium salts.

Ammonium salts	$LiCoO_2$	NCM622	$LiMn_2O_4$
NH_4Cl	Co_3O_4	MnO(OH), Unknow	$LiMn_2O_4$, Mn_3O_4
$(NH_4)_2SO_4$	Co_3O_4	MnO(OH), Unknow	MnO_2, Mn_5O_8
$(NH_4)_2CO_3$	Co_3O_4, Li_2CO_3	MnO(OH), Unknow	$LiMn_2O_4$, $MnCO_3$
NH_4HSO_4	$LiCoO_2$, Co_3O_4	MnO(OH), Unknow	MnO_2
NH_4HCO3	Co_3O_4	MnO(OH), Unknow	$LiMn_2O_4$
$(NH_4)_2SO_3 \cdot H_2O$	Co_3O_4	MnO(OH), Unknow	MnO_2, Mn_5O_8
$(NH_4)_3PO_4 \cdot 3H_2O$	Co_3O_4, Li_3PO_4	MnO(OH), Unknow	$LiMn_2O_4$, $LiMnPO_4$
$(NH_4)_2HPO_4$	Co_3O_4, Li_3PO_4	MnO(OH), Unknow	$LiMnPO_4$
$NH_4H_2PO_4$	$LiCoPO_4$	MnO(OH), Unknow	$LiMnPO_4$
NH_4F	Co_3O_4	MnO(OH), Unknow	MnO_2, LiF, (NH_4)MnF
NH_4HCO_2	Co_3O_4, $CoCO_3$	MnO(OH), $CoCO_3$, Unknow	Mn_3O_4, $MnCO_3$
NH_4OAc	Co_3O_4	MnO(OH), Unknow	$LiMn_2O_4$, Mn_3O_4,

			MnO_2
$C_6H_5O_7(NH_4)_3$	Co_3O_4, $CoCO_3$	MnO_2, $CoCO_3$	$MnCO_3$
$NH_3{\cdot}H_2O$	$LiCoO_2$	NCM622	$LiMn_2O_4$

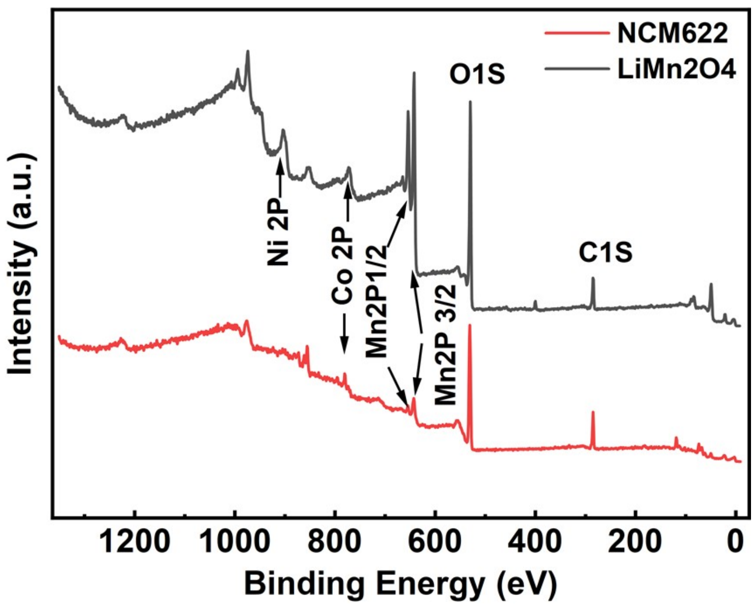

Fig. S11 XPS spectra of the products obtained from NCM622 and $LiMn_2O_4$ treated by $(NH_4)_2SO_4$ (reaction condition: 220C-0.73N-4h-3H for NCM622, 230C-0.73N-4h-3H for $LiMn_2O_4$).

The reaction equations of ammonium salt roasting for LMTO cathode materials

$NH_4Cl + 1/3LiCoO_2 = 1/3CoCl_2 + 1/3LiCl + 8/9NH_3 + 1/18N_2 + 2/3H_2O$ (46)

$1/2(NH_4)_2SO_4 + 1/3LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 = 1/15CoSO_4 + 1/5NiSO_4 + 1/15MnSO_4 + 1/6Li_2SO_4 + 1/18N_2 + 8/9NH_3 + 2/3H_2O$ (47)

$1/2(NH_4)_2SO_4 + 1/5LiMn_2O_4 = 2/5MnSO_4 + 1/10Li_2SO_4 + 1/10N_2 + 4/5NH_3 + 4/5H_2O$ (48)

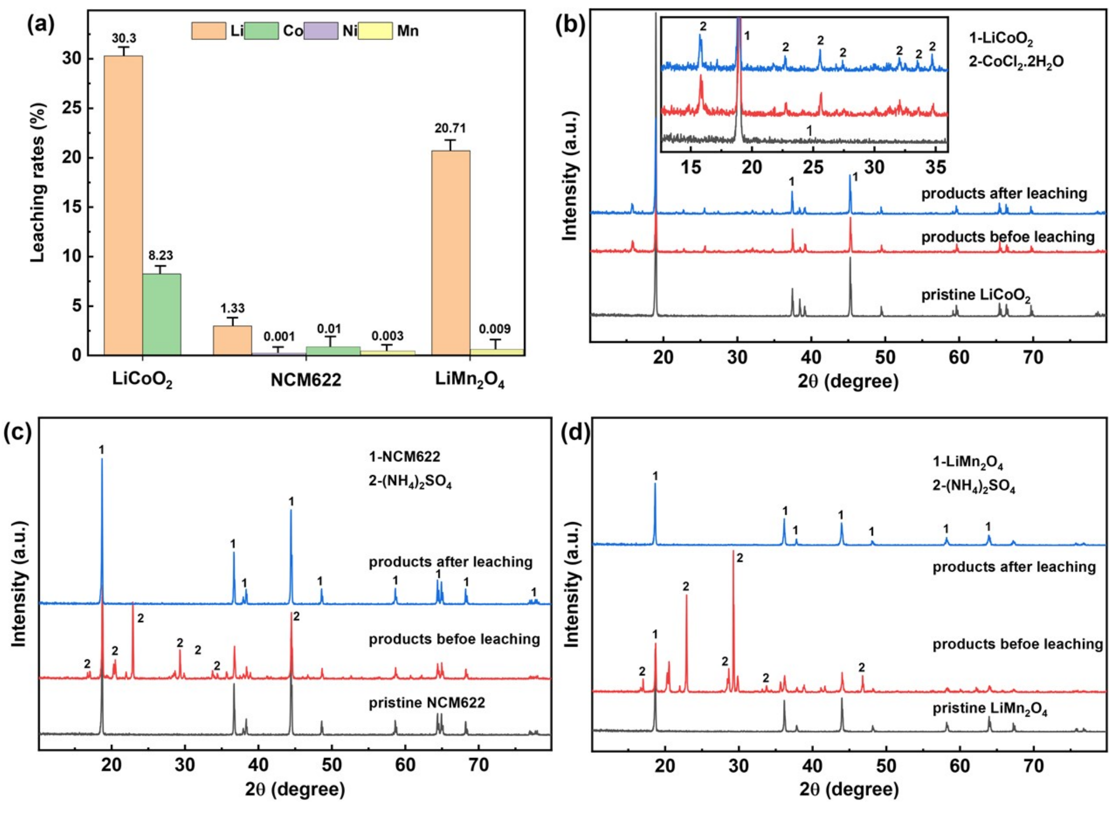

Fig. S12 (a) Leaching rates of Li, Ni, Co, and Mn of different types of cathode materials treated by ammonium salts in a hydrothermal reactor without adding H_2O (reaction condition: 220C-0.6N-4h-0H for $LiCoO_2/NH_4Cl$, 220C-0.73N-4h-0H for $NCM622/(NH_4)_2SO_4$, and 230C-0.73N-4h-0H for $LiMn_2O_4/(NH_4)_2SO_4$). (b-d) XRD patterns of the products of the cathode materials treated by ammonium salts without water in a hydrothermal reactor obtained from (a): (b) $LiCoO_2$ + NH_4Cl, (c) NCM622 + $(NH_4)_2SO_4$, (d) $LiMn_2O_4$ + $(NH_4)_2SO_4$).

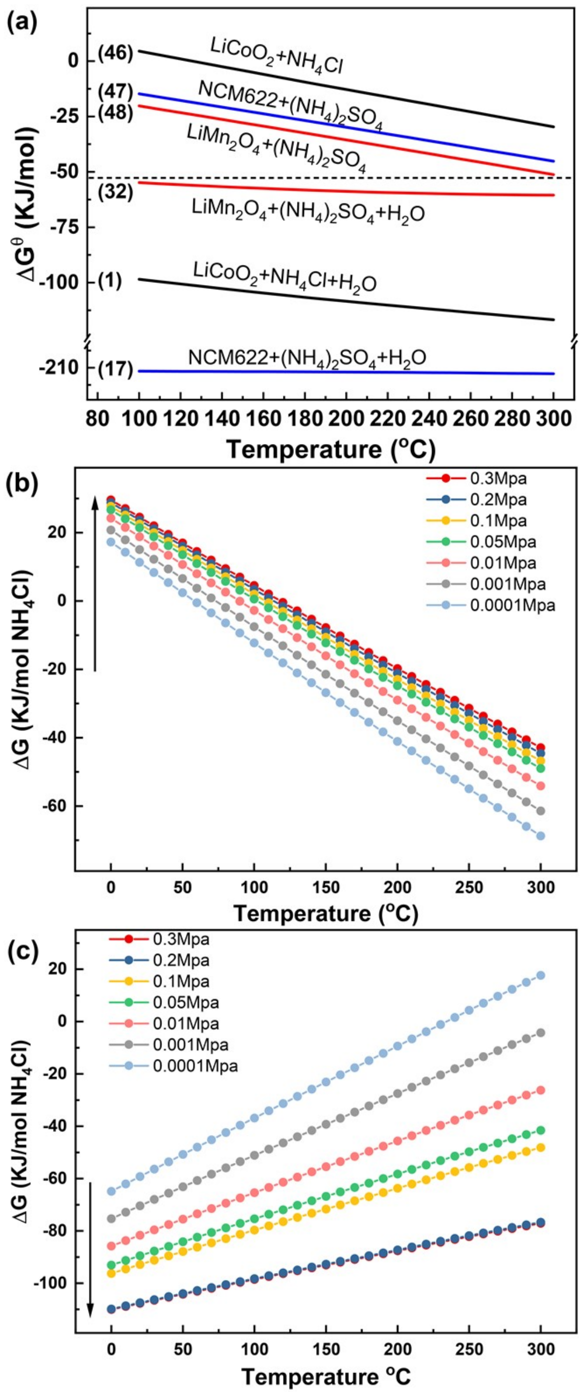

Fig. S13 (a) Profiles of Gibbs free energies as a function of temperature of ammonium roasting and ammonium reduction in a hydrothermal reactor by vapor thermal reduction. **Eqs.** 1, 17, and 32 correspond to the vapor thermal recovery for LMTO cathode, and **Eqs.** 46, 47, and 48 correspond to the ammonium salt roasting for LMTO cathode without the participation of H_2O. The effect of partial pressure of H_2O vapor inside the reactor on the thermal reduction of (b) $LiCoO_2$-NH_4Cl, **Eq.** 46, and (c) NH_4Cl +$LiCoO_2$ +H_2O, **Eq.** 1.

Tab. S7 Summary of the reaction conditions between ammonium salt roasting and leaching (the usage of chemicals and H_2O are calculated based on 1 g of LMTO cathode material).

Reaction system	Temperature (°C)	Usage of reagent (g)	Usage of H_2O (mL)	Reaction time (minute)	Products	Ref
NH_4Cl-LCO	350	2.0g		20	NH_4CoCl_3, Li_2CoCl_4	1
NH_4Cl-LCO	300	2.0g		20	NH_4CoCl_3, Li_2CoCl_4	2
$(NH_4)_2SO_4$-LCO	400	4.0g		120	$Li_2Co(SO_4)_2$, $LiSO_4$	3
$(NH_4)_2SO_4$-NCM622	400	4.0		90	$Li_2Co(SO_4)_2$, $MnSO_4$ $NiSO_4$	4
$(NH_4)_2SO_4$-LCO	600	3.0		45	$Li_2Co(SO_4)_2$, $CoSO_4$	5
$(NH_4)_2SO_4$-LMO	600	1.53		45	$Li_2Mn_2(SO_4)_3$, $MnSO_4$	6, 7
NH_4Cl-LCO	400	2.0		20	NH_4CoCl_3, $CoCl_2$, LiCl	8, 9
NH_4Cl-LMTO	550	1.9		30	Mn_3O_4, LiCl	10
$(NH_4)_2SO_4$-NCM	650	2.96		150	NiO, Co_3O_4, $MnSO_4$, Li_2SO_4, $Li_2Co(SO_4)_2$,	11
3M $(NH_4)_2SO_4$, 0.75M $(NH_4)_2SO_3$, 83 g L^{-1} LCO + LMO	180	5.82	12.05	120	$MnSO_4$, $CoSO_4$, $(NH_4)_2Mn(SO_4)_2.6H_2O$	12

367.5 g L^{-1} $NH_3 \cdot H_2O$, 140 g L^{-1} NH_4HCO_3, 63.24 g L^{-1} H_2O_2 15 g L^{-1} NCM523	30	38.05	66.7		$NiSO_4$, $CoSO_4$, MnCO3, Li_2CO_3	[13]
1 M $NH_3 \cdot H_2O$, 0.5 M $(NH_4)_2SO_3$, 1 M $(NH_4)_2CO_3$, 10 g L^{-1} NCM + LMO	80	18.9	100	60	$NiSO_4$, $CoSO_4$, MnO_2, Mn_3O_4, $MnCO_3$, Li_2CO_3	[14]
4M $NH_3 \cdot H_2O$, 1.5 NH_4Cl, 0.5 M Na_2SO_3, 10 g.L^{-1} NCM	80	28.31	100	300	$NiSO_4$, $CoSO_4$, $MnSO_4$, Mn_3O_4, $(NH_4)_2Mn(SO_3)_2.2H_2O$	[15]
1.5 M $NH_3 \cdot H_2O$, 1 M $(NH_4)_2SO_3$, 1 M NH_4HCO_3, 20 g L^{-1} LCNO	60	12.32	50	180	$NiSO_4$, $CoSO_4$, $MnSO_4$, Li_2SO_4, $(NH_4)_2Mn(SO_3)_2.2H_2O$	[16]
4 M $NH_3 \cdot H_2O$, 1.5 M NH_4Cl, 0.5M Na_2SO_3, 10 g L^{-1} NCM	80	40.1	100	600	$NiSO_4$, $CoSO_4$, $MnSO_4$, Li_2SO_4, $(NH_4)_2Mn(SO_3)_2.2H_2O$	[17]
6 M $NH_3 \cdot H_2O$,	150	33.9	100	30	$NiSO_4$, $CoSO_4$,	[18]

0.5 M NH_4Cl,	$MnSO_4$, Li_2SO_4,
0.5 M Na_2SO_3,	$(NH_4)_2Mn(SO_3)_2.2H_2O$
10 g L^{-1} LTMO	

M: mol/L

Economic and technic feasibility:

A detailed discussion about the economic and technic feasibility of recycling processes was below which has been added into Supporting information and highlighted.

Here, vapor thermal method was used to simulate recycling spent $LiCoO_2$ battery by a pilot batch process. Economic and energy consumption prospective of the vapor thermal approach was detailed discussed.

The recycling process in this study can be divided into four parts as shown in **Fig. S14**: NaCl-Discharging and Dismantling; Vapor thermal; Filtration ; Precipitation. It was assumed that 1 ton of spent $LiCoO_2$ batteries were treated by our green recycling process in China, the exchange rate between RMB and USD is 6.5(1$=6.5 CNY). The assumption of the cost of labor: the working day is 300 days per year (average 21 days per month) and the working time is about 8 hours every day. The average wage of per labor is 6200 CNY per year ($32 per day) in china. The assumption of the costs of electricity charge and other industrial raw material price are listed in **Tab. S8 (https://tradingeconomics.com/)**:

Tab. S8 The assumption of the costs of electricity charge and other industrial raw material price

Material	Price ($)
Spent $LiCoO_2$ battery	300/t
Water	0.92/t
NaCl	84.6/t
NH_4Cl	144/t
Na_2CO_3	265/t
Electricity	0.2/kWh
Li_2CO_3	15384/t
Co_3O_4	46152/t
Al	3076/t
Labor wage	32/day

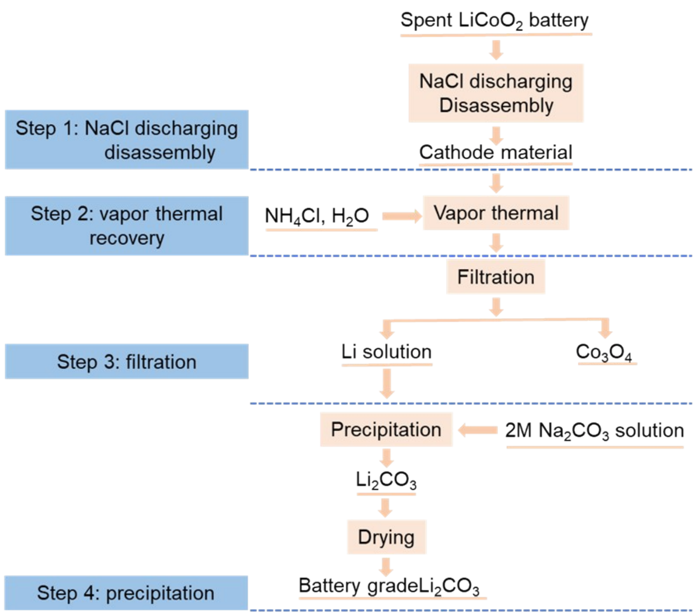

Fig. S14 A proposed vapor thermal process for the recycling of valuable metals from the spent $LiCoO_2$ Battery

And the energy consumption, the cost of energy, other industrial raw material, and labor are calculated as **Equations**. (49-51):

$C_e = P \times t \times c_e$ (49)

$C_m = m \times c_m$ (50)

$C_l = n \times c_l$ (51)

C_e, C_w, C_l are the cost of electricity, industrial raw material, labor, respectively. P, m, n are the equipment power (kW), the consumption of industrial raw material (t), and the number of workers. t is the working time of equipment. c_e, c_w, c_l is the electricity price, the price of industrial raw material, and wage of per labor. Finally, the energy consumption and the cost of every process and revenue of products in this study were calculated in detailed and then a profit was obtained by recycling 1 ton spent $LiCoO_2$ batteries with the current process as follows in China.

Step 1: NaCl-discharging and dismantling:

NaCl-discharging requirement: discharging in 5wt.% NaCl solution for 12 h, batteries/solution = 1:10 w/w (assume that the discharging is done at the night before); about 0.5 ton of NaCl and 2 ton of water were needed in the discharging process; one person, a set of automatic conveyor belts (P = 5kW, 2.0 m/s, maximum capacity=1000 m^3 /h) work for 8 hour every day.

$C_e = P \times t \times c_e = 5kW\ h^{-1} \times 8h \times \$0.2 = \$8$

$C_{water} = m \times c_{water} = 2 \times 0.92\$ = 1.84\$$

$C_{NaCl} = m \times c_{NaCl} = 0.5 \times 84.6\$ = 42.3\$$

$C_l = n \times c_l = 1 \times \$32 = \$32$

Dismantling: A small automated dismantling device was designed for spent $LiCoO_2$ batteries (P=8kW, maximum capacity=100kg/h, work time=10h)

$C_e = P \times t \times c_e = 8kW\ h^{-1} \times 10h \times \$0.2 = \$16$

$C_l = n \times c_l = 1 \times \$32 = \$32$

Energy consumption: **120 kW h-1**;

Water consumption: **2t**;

NaCl consumption: **0.5t**;

Cost of energy: **\$24**;

Cost of material (NaCl, water): **\$44.14**;

Total costs: **\$100.14**.

After this process, about 400kg of spent $LiCoO_2$ cathode scraps and 70.1 kg of Al foil can be obtained in this study.

Step 2: Vapor thermal:

One set of industrial reactor (Internal Electric Heater) (P=50Kw, capacity = 1000L, maximum working pressure 5 Mpa, heating temperature 300 ^oC,) was used to selectively recovery $LiCoO_2$. In this process, the obtained spent LiFePO4 cathode scraps were treated in batches of 4 by the reactor, which means the device needs to work 4 times every day. The working time including temperature rise and hold 240 ^{o}C is 4 hour every time. About 1.2 ton of water and 0.24 t of NH_4Cl was consumed.

$E_e = P \times t \times c_e = 50kW\ h^{-1} \times 4h \times \$0.2 \times 4 = \$160$

$C_{water} = m \times c_{water} = 1.2 \times 0.92\$ = 1.104\$$

$C_{NH4Cl} = m \times c_{NH4Cl} = 0.24 \times 144\$ = 34.56\$$

$C = n \times c_l = 1 \times \$32 = \$32$

Energy consumption: **800 kW h-1**;

Water consumption: **1.2t**;

NH4Cl consumption: **0.24t**;

Cost of energy: **$160**;

Cost of material (NH4Cl, water): **$35.664**;

Total costs: **$227.664**.

Step 3: Filtration and Drying:

Filtering requirement: A set of frame filter (P = 5Kw, maximum capacity = 30 m^2/per) is needed to work for 2 h. About 1 ton of water is consumed.

$E_e = P \times t \times c_e = 5kW\ h^{-1} \times 2h \times \$0.2 = \$2$

$C_{water} = m \times c_{water} = 2 \times 0.92\$ = 1.84\$$

$C_l = n \times c_l = 1 \times \$32 = \$32$

Drying requirement: A conveyor drier (P = 10Kw, maximum capacity = 200kg/per,) is needed to work for 4h to dry Co_3O_4 powder.

$$E_e = P \times t \times c_e = 10kW\ h^{-1} \times 4h \times \$0.2 = \$8$$

Energy consumption: **50 kW h-1**;

Water consumption: **2t**;

Cost of energy: **$10**;

Cost of material (water): **$1.84**;

Total costs: **$43.84**.

After this process, about 324.7 kg of Co_3O_4 powders and 600 Kg (13.9 g L^{-1} Li^+) filtrate can be obtained in this study.

Step 4: Precipitation, **filtration, and Drying**:

Precipitation: A set of glass lining reactors (Internal Electric Heater) (P = 5Kw, maximum capacity =500 L/per) are needed to respectively work for 1h including temperature rise and hold. About 1 ton water was consumed. 0.127 t of Na_2CO_3 is added into filtrate to precipitation Li_2CO_3.

$$E_e = P \times t \times c_e = 5kW\ h^{-1} \times 1h \times \$0.2 \times 1.2 = \$1.2$$

$$C_{water} = m \times c_{water} = 1 \times 0.92\$ = 0.92\$$$

$$C_{Na2CO3} = m \times c_{Na2CO3} = 0.127 \times 265\$ = 33.655\$$$

$$C_l = n \times c_l = 1 \times \$32 = \$32$$

Filtering requirement: A set of frame filter (P = 5Kw, maximum capacity = 30 m^2/per) is needed to work for 2 h. About 1 ton of water is consumed.

$E_e = P \times t \times c_e = 5kW\ h^{-1} \times 2h \times \$0.2 = \$2$

$C_{water} = m \times c_{water} = 1 \times 0.92\$ = 0.92\$$

After, **149.1 Kg of Li_2CO_3** is obtained.

Drying requirement: A conveyor drier (P = 10Kw, maximum capacity = 200kg/per,) is needed to work for 4h to dry Li_2CO_3 powder.

$E_e = P \times t \times c_e = 10kW\ h^{-1} \times 4h \times \$0.2 = \$8$

Energy consumption: **56 kW h-1**;

Water consumption: **2t**;

Na_2CO_3 consumption: **0.127t**;

Cost of energy: **\$11.2**;

Cost of material (water): **\$1.84**;

Cost of material (Na_2CO_3): **\$33.655**

Total costs: **\$78.695**.

After this process, about 149.1 kg of Li_2CO_3 powders can be obtained in this process. Thus, the whole energy consumption (E_T), the total cost of energy (C_E), the cost of the industrial raw material (C_M), and the total labor cost C_L in this study can be calculated:

$E_T = 120 + 800 + 50 + 56 = 1026kW\ h^{-1}$

$C_E = 1026kW\ h^{-1} \times \$0.2 = \$205.2$

$C_M = 1.84\$ + 1.104\$ + 1.84\$ + 1.84\$ = 6.624\$$

$C_L = 64\$ + 32\$ + 32\$ + 32\$ = 160\$$

The economic benefit for recycling spent $LiCoO_2$ battery by vapor thermal approach mainly comes from recycled Co_3O_4, Li_2CO_3, and Al foil. As shown in **Tab. S9**, the total raw material cost was about **\$578.14**, and **324.7 kg** of **Co_3O_4, 149.1 kg of Li_2CO_3, and 70.1 kg of Al foil** could be recycled from one ton of spent $LiCoO_2$ batteries. Detailed economic benefit analysis indicates a **\$16542.82** revenue by vapor thermal approach.

Table. S9 Economic and energy consumption prospective of the vapor thermal approach

Material	Price (\$)	Process (t)	Economic Benefit	Total revenue
Spent LiCoO2 battery	461/t	1	-461	
Water	0.92/t	7.2	-6.624	
NaCl	84.6/t	0.5	-42.3	16542.82
NH_4Cl	144/t	0.24	-34.56	
Na_2CO_3	265/t	0.127	-33.655	
Electricity	0.2/kWh	1026	-205.2	

Labor wage	32/day	5	-160
Li_2CO_3	15384/t	0.1491	2293.75
Co_3O_4	46152/t	0.3247	14976.78
Al	3076/t	0.0701	215.63

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