Supplementary materials

Table S1 Mass percentages of major elements in active cathode powders (wt.%)

Co	Ni	Mn	Li	Cu	Mg	Fe	Zn	Al	$[P]_T$	F
6.02	16.82	14.26	3.89	0.59	0.02	0.37	0.02	0.98	0.26	1.01

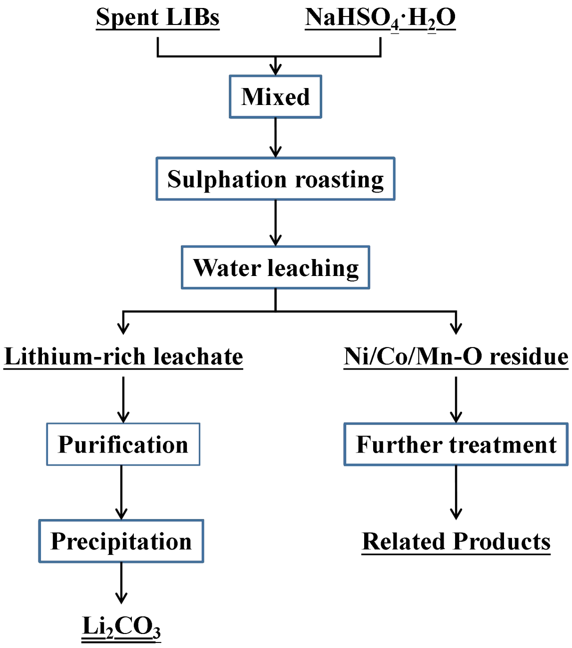

Figure S1 Schematic diagram of the selective lithium extraction process from spent lithium-ion batteries

Because of the lack of relevant thermodynamic data for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, the thermodynamic calculations were substituted with $LiCoO_2$, which has similar properties to it, and the ΔG-T relationship curves for the reactions that may occur during roasting are shown in Figure S2. As can be seen from Figure S2, the ΔG_θ for the reactions shown in Equations (1)-(7) are all less than zero when the temperature is raised above 500 °C, indicating that above this temperature, all the reactions shown can occur. At the same temperature, Equation (6) has a more negative ΔG value than Equation (7), indicating that the selective reaction of Equation (6) can be achieved by controlling the amount of $NaHSO_4 \cdot H_2O$ added, which theoretically argues that the use of $NaHSO_4 \cdot H_2O$ as a sulphation-assisted roasting agent can achieve the sulphate conversion of lithium from spent cathode powder while the transition metal is converted to oxide.

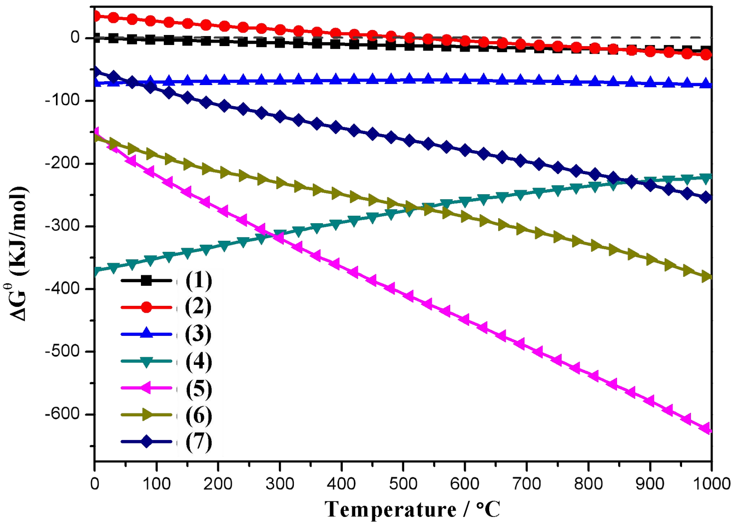

Figure S2 Relationship curves for ΔG_θ-T of $LiCoO_2$ under different sulphate roasting

$$NaHSO_4 \cdot H_2O = NaHSO_4 + H_2O(g) \tag{1}$$

$$2NaHSO_4 = Na_2SO_4 + H_2O(g) + SO_3(g) \tag{2}$$

$$4LiCoO_2 + 2SO_3(g) = 2Li_2SO_4 + 4CoO + O_2(g) \tag{3}$$

$$12LiCoO_2 + 6SO_3(g) = 6Li_2SO_4 + 4Co_3O_4 + O_2(g) \tag{4}$$

$$12LiCoO_2 + 12NaHSO_4 \cdot H_2O = 6Li_2SO_4 + 6Na_2SO_4 + 4Co_3O_4 + 18H_2O(g) + O_2(g) \tag{5}$$

$$12LiCoO_2 + 12NaHSO_4 = 6Li_2SO_4 + 4Co_3O_4 + 6Na_2SO_4 + 6H_2O(g) + O_2(g) \tag{6}$$

$$4LiCoO_2 + 12NaHSO_4 = 2Li_2SO_4 + 4CoSO_4 + 6Na_2SO_4 + 6H_2O(g) + O_2(g) \tag{7}$$

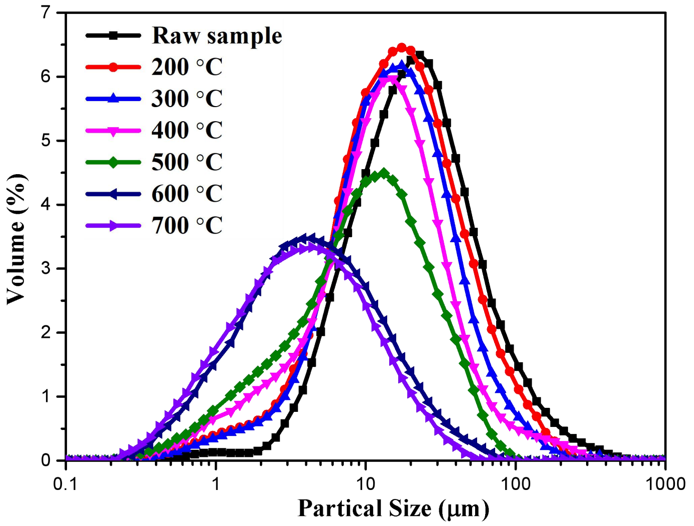

Figure S3 Particle size distribution curve of water leaching residue at various roasting temperatures

Table S2 Concentration of major ions in lithium enrichment solutions

Element	Li	Ni	Co	Mn
c/ppm	9450	1.2	0.35	3.4
c/($mol\cdot L^{-1}$)	1.35	--	--	--

Note: --represents the concentration of ions lower 0.0001 mol/L in the solution

As shown in Table S3, to find the optimal conditions for Li^+ and CO_3^{2-} removal by precipitation method from the leachate, detailed researches of the thermodynamic properties of the Li^+-CO_3^{2-}-H_2O systems were done. The equilibrium constant values were taken from the hand-book of chemistry edited by Kotrly′ [1] and Spaeight [2] respectively. In the second stage, various combinations of these equations were considered depending on the nature of the solid phases that may be in equilibrium with the solution.

Table S3 Thermodynamic parameters of the solution system at different temperatures (K) for Li^+-CO_3^{2-}-H_2O

No.	Equilibrium reactions	Equilibrium constants (K^*)	logK^* (298)	logK^* (313)	logK^* (333)	logK^* (353)	logK^* (363)
(1)	$H_2O = H^+ + OH^-$	$K^*= [H^+][OH^-]$	-14	-13.54	-13	-12.6	-12.43
(2)	$HSO_4^- = H^+ + SO_4^{2-}$	$K^*= [SO_4^{2-}][H^+]/[HSO_4^-]$	-1.99	-2.13	-2.42	-2.72	-2.87
(5)	$CO_3^{2-}+H^+=HCO_3^-$	$K^*= [HCO_3^-]/\{[CO_3^{2-}][H^+]\}$	10.35	10.26	10.186	10.17	10.16
(6)	$HCO_3^-+H^+=H_2CO_3$	$K^*= [H_2CO_3]/\{[HCO_3^-][H^+]\}$	6.23	6.15	6.059	5.98	5.9
(7)	$Li^+ + OH^- = LiOH_{(aq)}$	$K^*=[LiOH_{(aq)}]/\{[Li^+][OH^-]\}$	0.314	0.32	0.345	0.38	0.4
(8)	$Li^+ + SO_4^{2-} = LiSO_4^-$	$K^*=[LiSO_4^-]/\{[Li^+][SO_4^{2-}]\}$	0.89	0.877	0.882	0.9	0.92
(9)	$Li_2CO_3=2Li^+ + CO_3^{2-}$	$K^*= [Li^+]^2[CO_3^{2-}]$	-3.06	-3.4	-3.66	-3.91	-4.04
	Equation of conservation of matter in solution systems						
(10)	$[C]_T=[CO_3^{2-}]+[HCO_3^-]+[H_2CO_3]$						
(11)	$[Li]_T = [Li^+] + [LiOH_{(aq)}] + [LiSO_4^-]$						
(12)	$2\{[Li]_{T\text{-initial}} - [Li]_T\}= [C]_{T\text{-initial}} - [C]_T$						

Note: $[Li]_{T\text{-initial}}$ and $[C]_{T\text{-initial}}$ represent the initial total lithium fraction concentration and the total carbon fraction concentration in the solution

Reference

[1] KOTRLY ´ S, SUCHA L. Handbook of Chemical Equilibria in Analytical Chemistry [M]. Ellis Horwood, Chichester, 1985.

[2] SPEIGHT J G, LANGE N A. Lange’s Handbook of Chemistry [M]. 16th ed. McGraw-Hill Professional, Maidenhead, 2004.