SUPPORTING INFORMATION

Ethanol-Aerosol–Derived In-Situ Syngas Roasting for Lithium Recovery from Spent Layered Oxide Cathodes

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Table S1 The content of metal elements in the spent NCM523 powder.

Composition	Li	Ni	Co	Mn	Al
Content (wt%)	5.61	29.64	11.86	16.63	0.10

Table S2 Purity analysis of recovered Li_2CO_3 under optimized conditions.

Composition	Li_2CO_3	Ni	Co	Mn	Al	Na
Content (wt%)	99.65	ND	ND	ND	ND	0.02

Note: Li_2CO_3 content was calculated from ICP-measured Li. Other species are reported as elemental contents. ND: below the ICP detection limit.

Note S1 Gas composition analysis of the pyrolysis products

A pump-drawn composite gas detector was employed to detect the concentration of the syngas generated by 1vol.% ethanol (EtOH) under the conditions of N_2 flow rate of 100 mL min^{-1} and a calcination temperature of 600 °C, with the measured concentrations of H_2 and CO found to be approximately 1200 ppm and 600 ppm, respectively. Using these experimentally determined conditions and concentration data, the following calculations serve to demonstrate that at 100 mL min^{-1}, the amount of EtOH aerosol introduced was theoretically sufficient to fully reduce 1 g of cathode powder per batch.

1. Assumptions & Basic data

1.1 Core assumptions

Reaction: $C_2H_5OH + H_2O = 2CO + 4H_2$ (1 mol EtOH → 6 mol reducing gas);

Reduction stoichiometry: 1 mol $LiCoO_2$ (Co^{3+}→Co^{2+}) requires 0.5 mol reducing gas (H_2/CO, 2 mol e^- per mol);

Atomization efficiency: EtOH feeding rate ∝ EtOH concentration; Feeding time = 30 min.

1.2 Basic data

$Q_{N_2,\,25\,°C} = 100$ mL min^{-1}, $T = 600\ °C = 873\ K$, $T_0 = 25\ °C = 298\ K$;

$C_{H_2,\,1\%} = 1200 \times 10^{-6}$, $M_{LiCoO_2} = 98$ g mol^{-1}, $P = 1$ atm;

$m_{LiCoO_2} = 1$ g.

2. Total reducing gas production (30 vol.% EtOH, 30 min)

2.1 N_2 flow rate at 873 K

$$Q_{N_2,\,873\,K} = Q_{N_2,\,298\,K} \times \frac{T}{T_0} = 100 \times \frac{873}{298} \approx 293 \text{ mL min}^{-1}$$

2.2 $n_{H_2,\ 1\%}$ (1 vol.% EtOH)

$$Q_{H_2,\ 1\%} = C_{H_2,1\%} \times Q_{N_2,\ 873\ K} = 1200 \times 10^{-6} \times 293 \approx 0.352 \text{ mL min}^{-1}$$

$$n_{H_2,\ 1\%} = \frac{P \times Q_{H_2,1\%}}{R \times T} = \frac{1 \times 0.352}{8.314 \times 873} \approx 4.8 \times 10^{-5} \text{ mol min}^{-1}$$

2.3 $n_{EtOH,\ 1\%}$ & $n_{EtOH,\ 30\%}$

$$n_{EtOH,\ 1\%} = \frac{n_{H_2,\ 1\%}}{4} = \frac{4.8 \times 10^{-5}}{4} = 1.2 \times 10^{-5} \text{ mol min}^{-1}$$

$$n_{EtOH,\ 30\%} = n_{EtOH,\ 1\%} \times 30 = 1.2 \times 10^{-5} \times 30 = 3.6 \times 10^{-4} \text{ mol min}^{-1}$$

2.4 $n_{Total\ reducing\ gas}$

$$n_{Total\ reducing\ gas} = n_{EtOH,\ 30\%} \times 6 \times t = 3.6 \times 10^{-4} \times 6 \times 30 \approx 6.5 \times 10^{-2} \text{ mol}$$

3. Required reducing gas for 1 g $LiCoO_2$

3.1 n_{LiCoO_2}

$$n_{LiCoO_2} = \frac{m_{LiCoO_2}}{M_{LiCoO_2}} = \frac{1}{98} \approx 1.0 \times 10^{-2} \text{ mol}$$

3.2 $n_{Required\ reducing\ gas}$

$$n_{Required\ reducing\ gas} = n_{LiCoO_2} \times 0.5 = 1.0 \times 10^{-2} \times 0.5 = 5.0 \times 10^{-3} \text{ mol}$$

4. Feasibility verification

$n_{Total\ reducing\ gas}(6.5 \times 10^{-2}\ mol) \gg n_{Required\ reducing\ gas}(5.0 \times 10^{-3}\ mol)$ (≈12.7-fold excess; sufficient even with gas loss.)

Conclusion: H_2 and CO from 30 vol.% ethanol (30 min feeding) completely reduce 1 g $LiCoO_2$ to CoO.

Note S2 The calculations of overall S/L ratio of acid–water sequential leaching.

A certain mass of roasted powder was subjected to acid leaching, where the S/L ratio was maintained at 300 g L^{-1}, resulting in the leaching of approximately 75% of lithium. After filtration, the filter residue was weighed, and its mass accounted for 82.1% of the total mass of the original powder. Subsequently, the filter residue was subjected to water leaching with a S/L ratio of 200 g L^{-1}, resulting in a final lithium leaching rate of 97.3%. Using these experimentally determined conditions and data, the following calculations serve to demonstrate that the overall S/L rate is 135 g L^{-1}.

1.Basic data

Let the mass of initial roasted powder (total solid) be "$m_{\text{total, solid}}$", and then the mass of acid-leached filter residue (m_{residue}) = 0.821 $m_{\text{total, solid}}$.

The S/L ratio for acid leaching (R_1) = 300 g L^{-1};

The S/L ratio for the subsequent water leaching (R_2) = 200 g L^{-1}.

2. Calculation process

2.1 Calculate liquid volume for acid leaching (V_1)

The S/L ratio is defined as:

$$R = \frac{m_{solid}}{V_{liquid}}$$

Rearranged to solve for liquid volume:

$$V_{liquid} = \frac{m_{solid}}{R}$$

For acid leaching, the solid is the initial powder ($m_{\text{solid}} = m_{\text{total, solid}}$), so:

$$V_1 = \frac{m_{total,\, solid}}{R_1}$$

2.2 Calculate liquid volume for the subsequent water leaching (V_2)

$$V_2 = \frac{m_{residue}}{R_2} = 0.821 \times \frac{m_{total,\, solid}}{R_2}$$

2.3 Calculate total liquid volume ($V_{\text{total, liquid}}$)

$$V_{total,liquid} = V_1 + V_2 = m_{total,\, solid}(\frac{1}{R_1} + \frac{0.821}{R_2})$$

2.4 Calculate total S/L ratio (R_{total})

Based on the definition of total S/L ratio:

$$R_{total} = \frac{m_{total,solid}}{V_{total,liquid}}$$

Substitute the values of total solid mass and total liquid volume:

$$R_{total} = \frac{m_{total,solid}}{m_{total,\, solid}(\frac{1}{R_1} + \frac{0.821}{R_2})} = \frac{1}{\frac{1}{R_1} + \frac{0.821}{R_2}} = \frac{1}{\frac{1}{300\ g\ L^{-1}} + \frac{0.821}{200\ g\ L^{-1}}} \approx 134.4\ g\ L^{-1}$$

3. Conclusion

The total S/L ratio of the acid–water sequential leaching is approximately 134.4 g L^{-1} (minor deviations may occur due to rounding during intermediate calculations, which is within the acceptable error range).

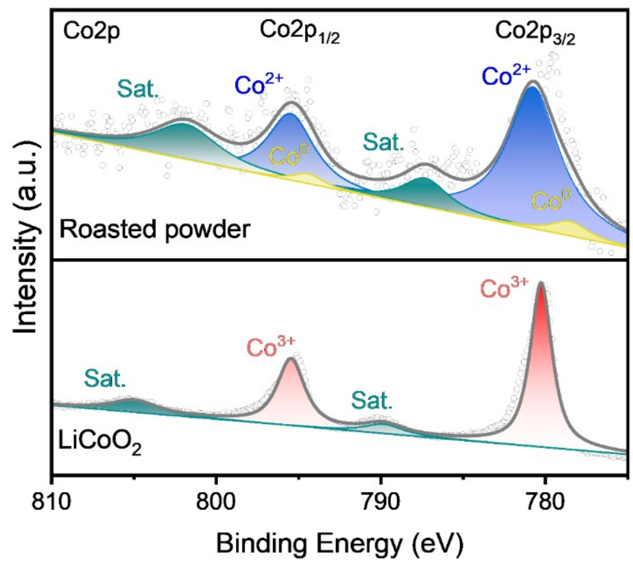

Fig. S1 Co 2p XPS spectra of $LiCoO_2$ and the roasted powder

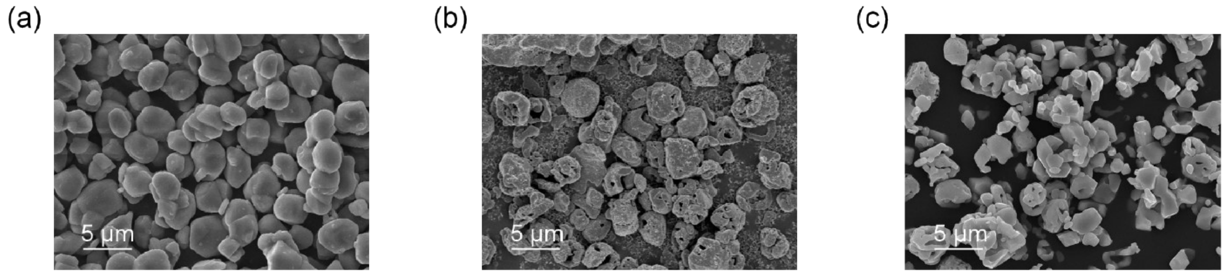

Fig. S2 (a–c) SEM image of (a) $LiCoO_2$ powder, (b) roasted powder, (c) leaching residue.

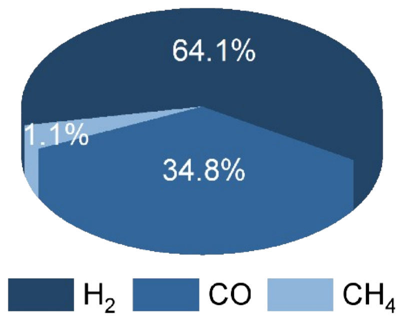

Fig. S3 The major gaseous products of ethanol aerosol at 600 °C

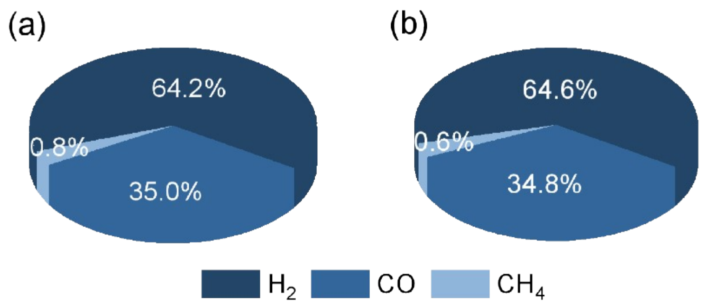

Fig. S4 The major gaseous products of ethanol aerosol at (a) 700 °C, (b) 800 °C.

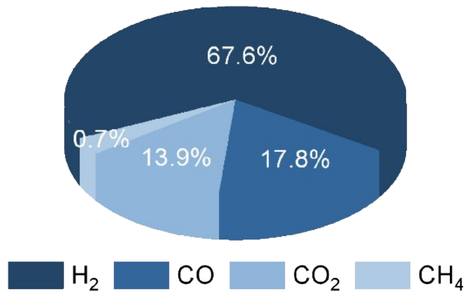

Fig. S5 The off-gas after ethanol aerosol reduction roasting at 600 °C in the presence of cathode powder

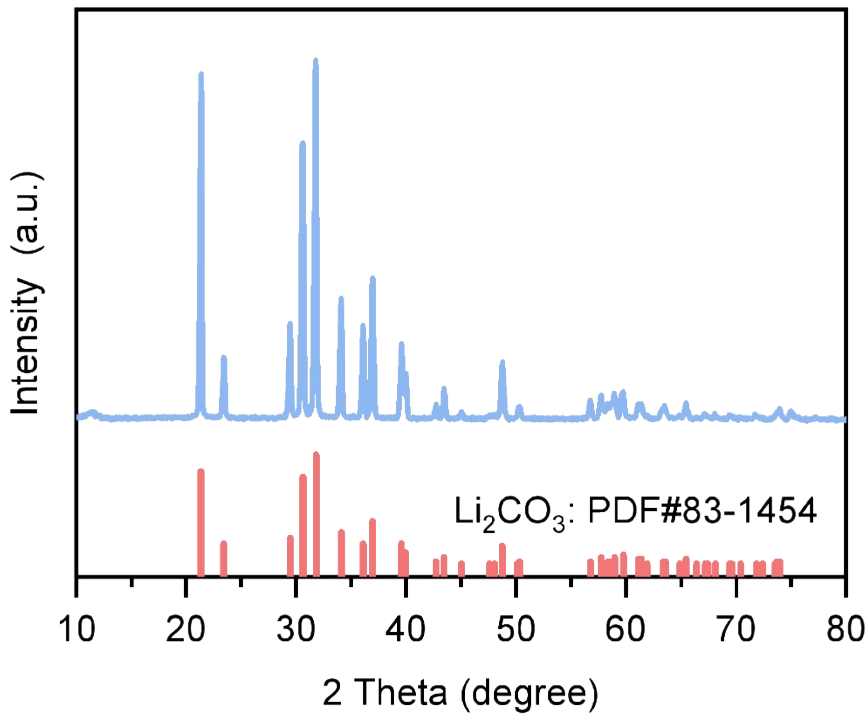

Fig. S6 XRD pattern of recovered Li_2CO_3.

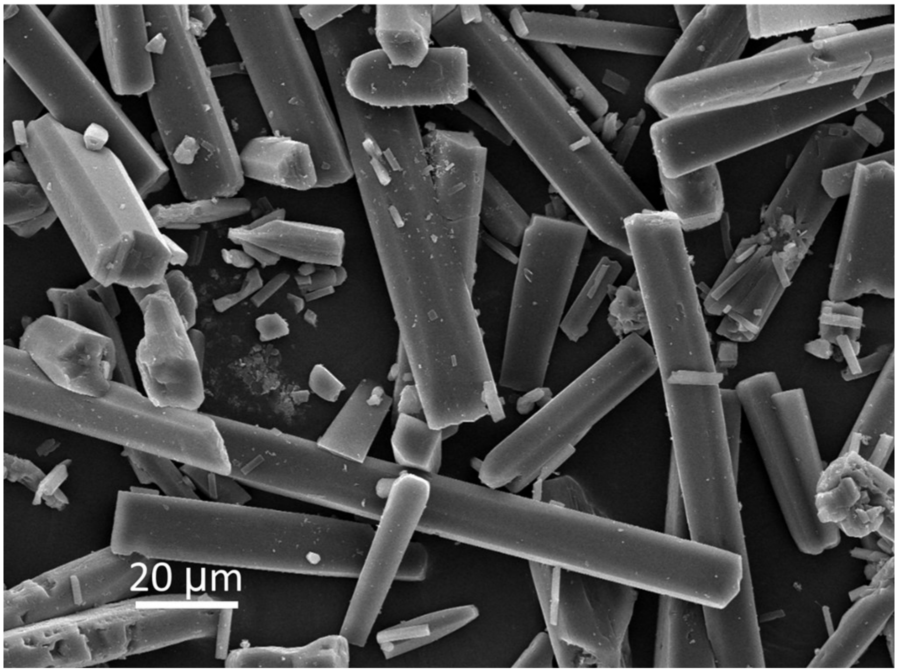

Fig. S7 SEM image of recovered Li_2CO_3.

Note: Li_2CO_3 presenting as slender rods (~5–10 μm in diameter, 30–100 μm in length).