

## Supplementary Material

# Recycling of Li, Co from spent LiCoO<sub>2</sub> cathode materials through a low temperature urea-assisted sulfation roasting approach

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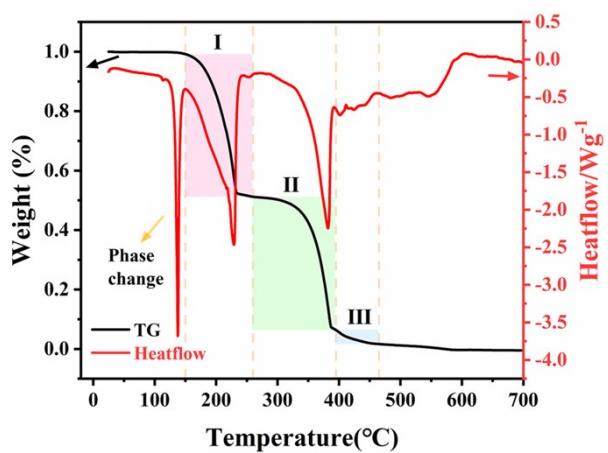
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**Table S1.** Several representative cases of salt-thermal methods for recycling valuable metal elements from cathode materials by roasting approaches

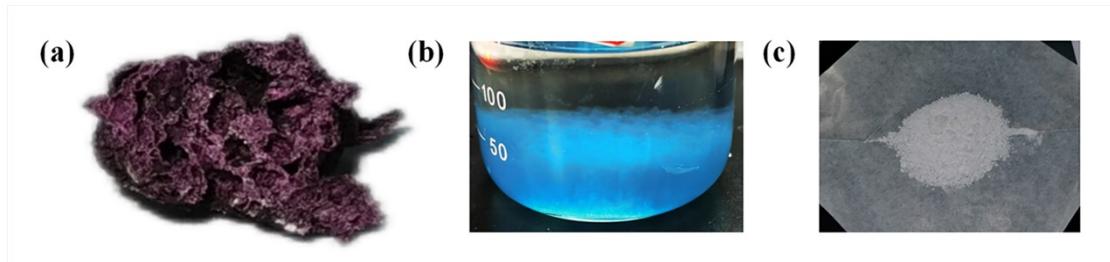
| Roasting agent                                  | Reaction condition   | Products and recovery efficiency  | Ref. |
|---|--|---|------|
| NiSO <sub>4</sub>                               | NCM111 : NiSO <sub>4</sub> ·6H <sub>2</sub> O = 2 : 1 (mole ratio), 550 °C, 60 min, air.                           | Li <sub>2</sub> SO <sub>4</sub> , NiO, Ni <sub>0.66</sub> Co <sub>0.66</sub> Mn <sub>0.66</sub> O <sub>3</sub> ; 96.42% for Li, M< 3.62% (M = Ni, Co, and Mn)                 | 1    |
| ZnSO <sub>4</sub>                               | LiMn <sub>2</sub> O <sub>4</sub> : ZnSO <sub>4</sub> ·6H <sub>2</sub> O = 1 : 1 (mole ratio), 550 °C, 60 min, air. | Li <sub>2</sub> SO <sub>4</sub> , nano ZnMn <sub>2</sub> O <sub>4</sub> as Li <sup>+</sup> anode  | 2    |
| CoSO <sub>4</sub>                               | LiCoO <sub>2</sub> : CoSO <sub>4</sub> ·7H <sub>2</sub> O = 1 : 1 (mole ratio), 550 °C, 60 min, air.               | Li <sub>2</sub> SO <sub>4</sub> , nano-octahedral Co <sub>3</sub> O <sub>4</sub> as Li <sup>+</sup> anode 987.2 mA h g <sup>-1</sup> at 100st cycle at 0.05 A g <sup>-1</sup> | 2    |
| NaHSO <sub>4</sub>                              | LiCoO <sub>2</sub> : NaHSO <sub>4</sub> = 1 : 1.4 (mass ratio) 600 °C, 30 min, air                                 | Li <sub>2</sub> SO <sub>4</sub> , Co <sub>3</sub> O <sub>4</sub> 72.56% for Li, 0.53% for Co  | 3    |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | LiCoO <sub>2</sub> : (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> = 1 : 2.2 (mole ratio) 600 °C, 45 min, air    | Li <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub> , CoSO <sub>4</sub> ; 99.5% for Li, 8.53% for Co  | 4    |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | LiCoO <sub>2</sub> : (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> = 1 : 4 (mass ratio) 400 °C, 120 min, Ar      | Li <sub>2</sub> SO <sub>4</sub> , CoSO <sub>4</sub> , Li <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub> ; over 98% for both Li and Co   | 5    |

|                              |  |  |   |
|------------------------------|--|--|---|
| $(\text{NH}_4)_2\text{SO}_4$ | NCM622 : $(\text{NH}_4)_2\text{SO}_4 = 1 : 4$<br>(mass ratio) 350 °C, 90 min,<br>air         | $\text{Li}_2\text{SO}_4$ , $\text{NiSO}_4$ , $\text{CoSO}_4$ , $\text{MnSO}_4$ ;<br>99.2%, 99.4%, 98.8%, and<br>98.5% for Li, Ni, Co, Mn | 6 |
| $\text{Na}_2\text{CO}_3$     | LFP : $\text{Na}_2\text{CO}_3$ : graphite = 1 : 2 (mole ratio), 900 °C, 4 h,<br>$\text{N}_2$ | Fe, $\text{NaLi}_2\text{PO}_4$ , $\text{LiNa}_5(\text{PO}_4)_2$ , Li<br>for 96.4%; $\text{Fe}_3\text{O}_4$                               | 7 |

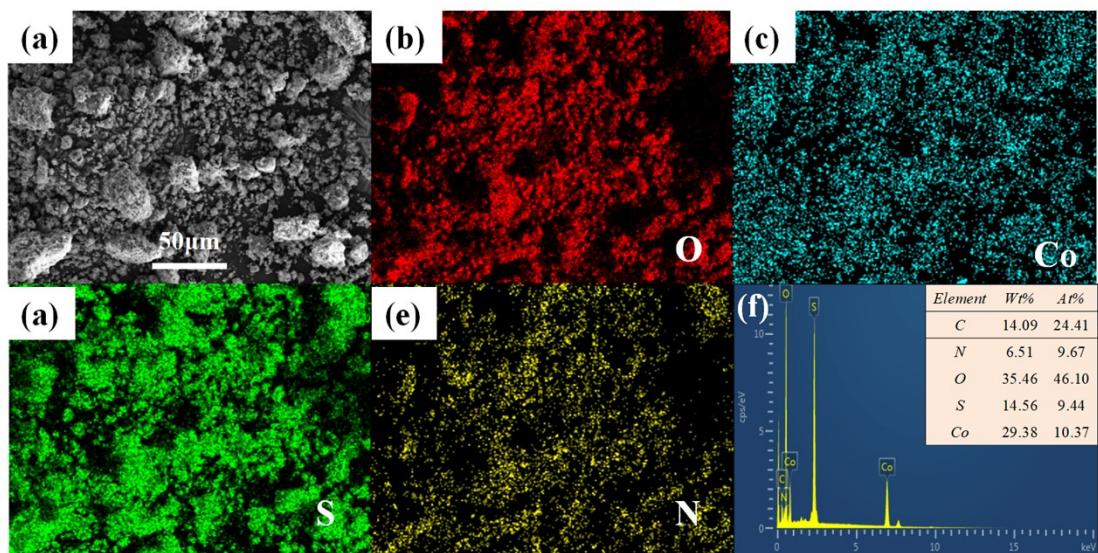
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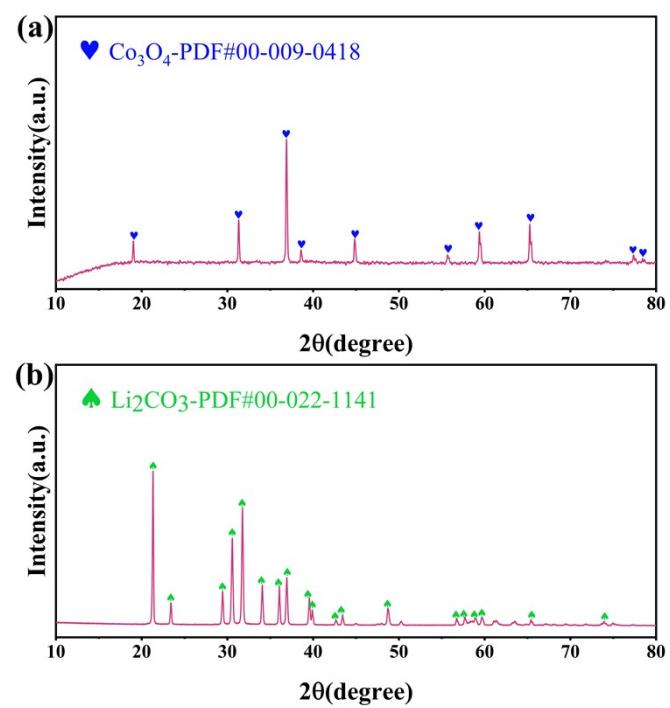
**Fig. S1.** TG curves of pure urea.



**Fig. S2.** Physical picture of (a) the sample after urea-assisted sulfation roasting; (b) the precipitated  $\text{CoCO}_3$ ; (c) the concentrated precipitated  $\text{Li}_2\text{CO}_3$ .



**Fig. S3.** SEM images of (a) roasted sample; (b-e) the corresponding EDS mapping and (f) content distribution for C, N, O, S and Co in roasted sample.



**Fig. S4.** XRD patterns of (a)  $\text{Co}_3\text{O}_4$  obtained by calcination; (b) concentrated and dried  $\text{Li}_2\text{CO}_3$ .

## Reference

- 1 J. Lin, C. Cui, X. Zhang, E. Fan, R. Chen, F. Wu and L. Li, *Journal of Hazardous Materials*, 2022, **424**, 127757.
- 2 J. Lin, E. Fan, X. Zhang, R. Chen, F. Wu and L. Li, *Advanced Energy Materials*, 2022, **12**, 2103288.
- 3 D. Wang, X. Zhang, H. Chen and J. Sun, *Minerals Engineering*, 2018, **126**, 28–35.
- 4 S. He, B. P. Wilson, M. Lundström and Z. Liu, *Journal of Cleaner Production*, 2020, **268**, 122299.
- 5 Y. Tang, B. Zhang, H. Xie, X. Qu, P. Xing and H. Yin, *Journal of Power Sources*, 2020, **474**, 228596.
- 6 Y. Tang, X. Qu, B. Zhang, Y. Zhao, H. Xie, J. Zhao, Z. Ning, P. Xing and H. Yin, *Journal of Cleaner Production*, 2021, **279**, 123633.
- 7 B. Zhang, X. Qu, X. Chen, D. Liu, Z. Zhao, H. Xie, D. Wang and H. Yin, *Journal of Hazardous Materials*, 2022, **424**, 127586.