

## Supporting Information

### Electrolyte-assisted low-voltage decomposition of $\text{Li}_2\text{C}_2\text{O}_4$ for efficient cathode pre-lithiation in lithium-ion batteries

#### Experimental Section:

##### Synthesis of re- $\text{Li}_2\text{C}_2\text{O}_4$ :

3.0g of commercial lithium oxalate ( $\text{Li}_2\text{C}_2\text{O}_4$ , Macklin,  $\geq 98.0\%$ ) was added in 150 mL deionized water. After slowly stirring for 30 min with ultrasound, the mixture was slowly poured into 150 mL anhydrous ethanol (99.5%) and the white power was obtained by filtration and vacuum drying.

##### Preparation of commercial $\text{Li}_2\text{C}_2\text{O}_4$ and re- $\text{Li}_2\text{C}_2\text{O}_4$ electrodes

Commercial  $\text{Li}_2\text{C}_2\text{O}_4$  (or re- $\text{Li}_2\text{C}_2\text{O}_4$ ), SP (super p carbon) and PVDF (polyvinylidene fluoride) were mixed in NMP with the mass ratio of 6: 3: 1. Then the slurry was casted onto the aluminum foil and dried at  $120^\circ\text{C}$  for 10 h under vacuum. The electrodes were cut to  $\Phi 14$  mm sheets and pressed at the pressure of 10 MPa. The  $\text{Li}_2\text{C}_2\text{O}_4$  loading in electrodes was  $0.3\sim 0.45\text{mg cm}^{-2}$ .

##### Preparation of cathode and anode electrodes

For NCM electrode, the electrode composites of 80 wt.% NCM, 10 wt.% SP and 10 wt.% PVDF. For NCM(re- $\text{Li}_2\text{C}_2\text{O}_4$ ) electrode, the electrode composites of 76 wt.% NCM, 4 wt.% re- $\text{Li}_2\text{C}_2\text{O}_4$ , 10 wt.% SP and 10 wt.% PVDF. For anode electrode, the mass ratio of silicon-graphite, CMC-SBR and SP is 80:10:10.

All the electrode was made in the laboratory environment.

##### Electrochemical measurements

The CR2025 coin-type cells were assembled in a glove box under Ar atmosphere with celgard-2500 film as the separator and Li foil as the counter electrode. The baseline electrolyte was 1 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC)/diethyl dimethyl carbonate (DMC) (3/7 in volume ratio). The NO electrolyte was prepared by

adding 0.06M NaNO<sub>2</sub> to the baseline electrolyte. The Neware Battery Testing System (BST-5V20mA, China) was used to test the electrochemical performance for all cells and the test temperature was 28°C. The N/P ratio of full cells was controlled at 1.02-1.2. A CHI720 electrochemical workstation was used for the cyclic voltammetry (CV) measurement. The CV measurements for Si-G||Li half-cells in different electrolytes were measured on at a scan rate of 0.2 mV s<sup>-1</sup> from 0.01 ~ 2.5 V.

For both NCM||Li half-cells, NCM(re-Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)||Li half-cells and full-cells, the initial cycle is 0.05 C and the following two cycles is 0.1 C, where 1 C=200 mA g<sup>-1</sup>. After activation process, the current for following cycles is 0.5 C.

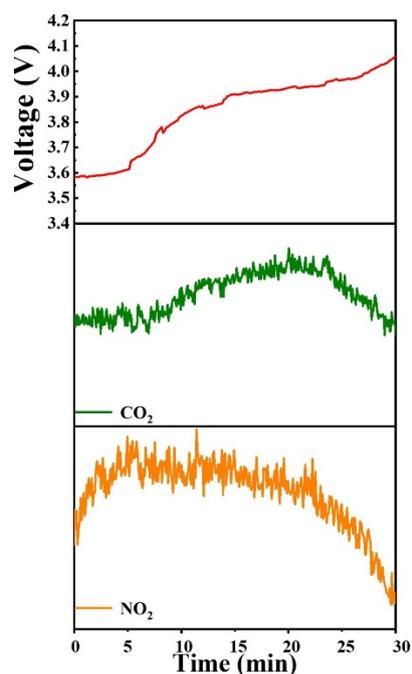
As for Si-G anode, the charge/discharge procedure for the initial 3 cycles is 0.1 C and 0.2 C for the following cycles in Si-G||Li half-cells (1 C=1000 mA g<sup>-1</sup>).

### **Physical characterization**

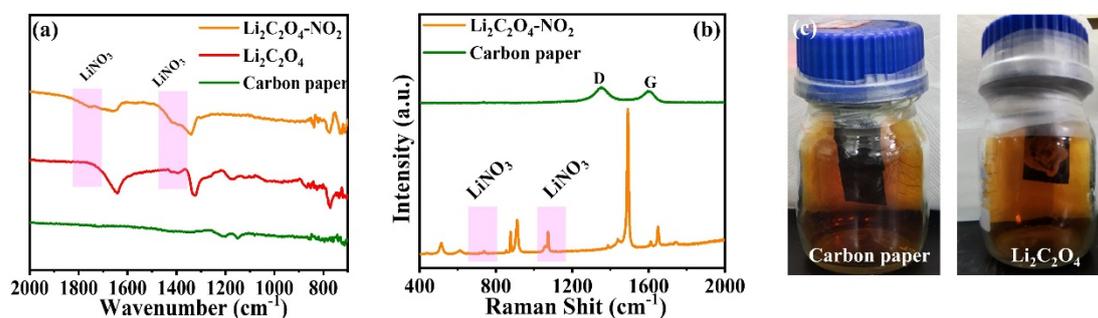
Scanning electron microscopy (SEM, Carl Zeiss MERLIN Compact, 10-20 kV) was performed to analyze the morphology and particle size of the materials and electrodes. X-ray diffraction (XRD) patterns were collected by a BPUKER/D2PHASER X-ray diffractometer (Germany) with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The X-ray photoelectron spectroscopy (XPS) was conducted for electrodes using a TESCALAB 250Xi instrument. The decomposition product of Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were collected by Raman spectrometer (Renishaw) and Bruker Vertex 70 FT-IR spectrometer (Germany).

### **DFT computation**

The Gaussian 09 software were used for DFT computation. In this article, the hybrid B3LYP functional<sup>1</sup> with 6-311G++ basis set<sup>2,3</sup> was used to optimize and calculate The LUMO and HOMO orbital energy levels.



**Figure S1** Voltage profile of commercial  $\text{Li}_2\text{C}_2\text{O}_4$  and in-situ gaseous evolution manners of  $\text{NO}_2$  and  $\text{CO}_2$  measured by DEMS as a function of time for commercial  $\text{Li}_2\text{C}_2\text{O}_4$  in  $\text{NO}$  electrolyte.



**Figure S2** The reaction products between commercial  $\text{Li}_2\text{C}_2\text{O}_4$  and  $\text{NO}_2$ . (a) FTIR spectra and (b) Raman spectra. (c) experimental equipment for the reaction between commercial  $\text{Li}_2\text{C}_2\text{O}_4$  and  $\text{NO}_2$ .

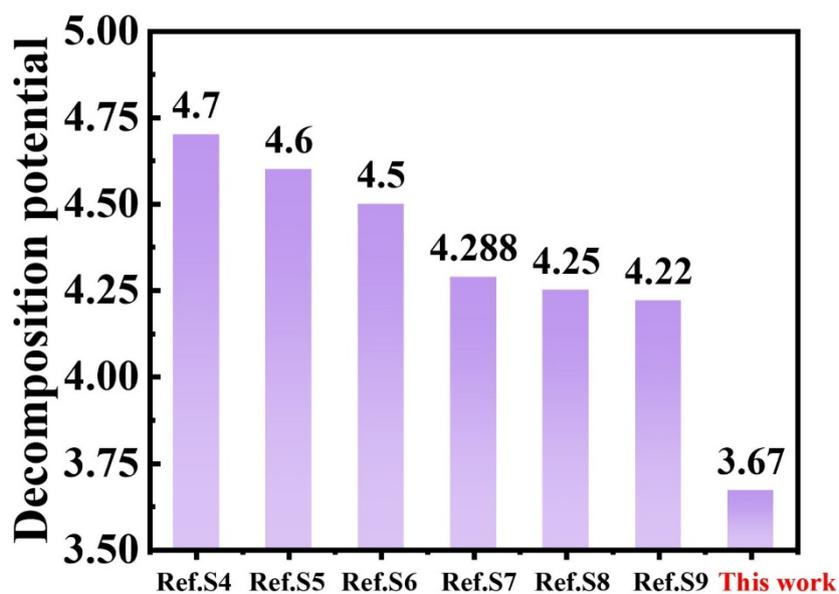


Figure S3 Comparison of the decomposition potential of  $\text{Li}_2\text{C}_2\text{O}_4$  in reported articles<sup>4-9</sup>.

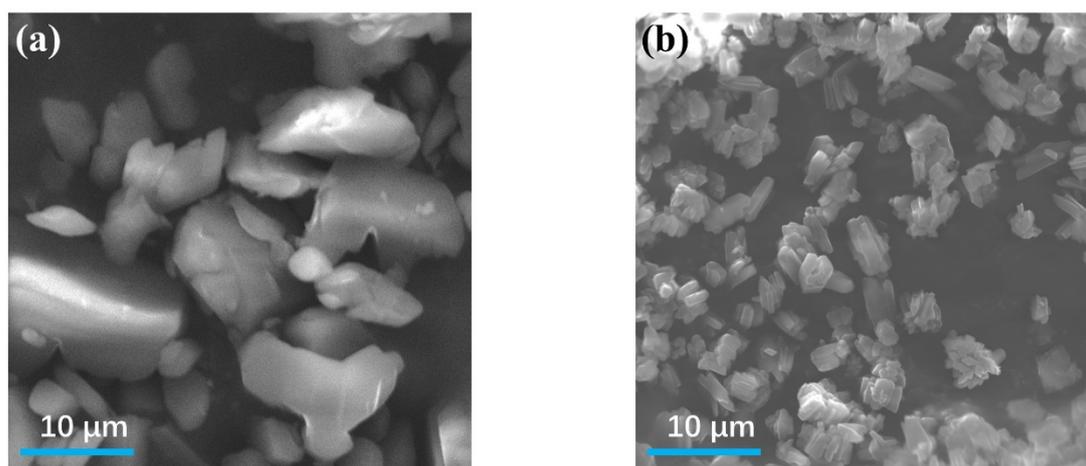


Figure S4 SEM images (a) commercial  $\text{Li}_2\text{C}_2\text{O}_4$ . (b) re- $\text{Li}_2\text{C}_2\text{O}_4$ .

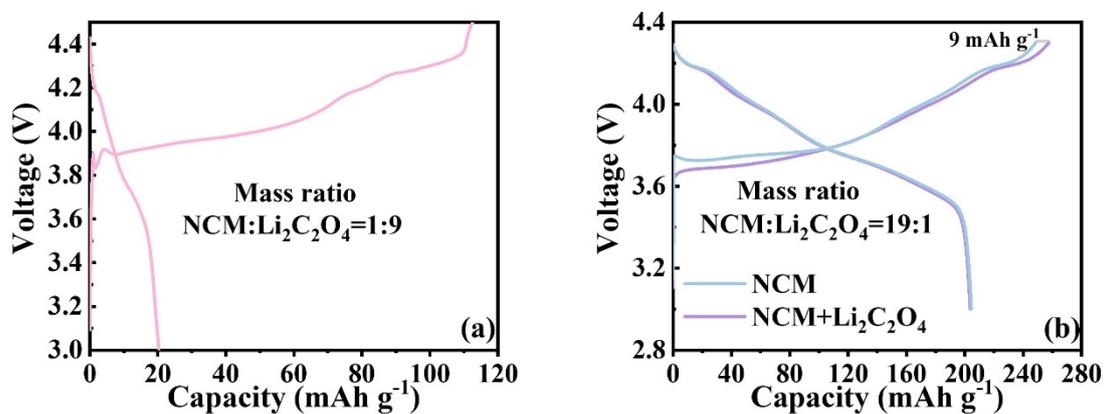


Figure S5 the 1st cycle voltage profile of different electrode in baseline electrolyte

with the mass ratio of NCM and  $\text{Li}_2\text{C}_2\text{O}_4$  of (a) 1:9 and (b) 19:1

### Note

The initial charge capacity in (a) is  $112.5 \text{ mA g}^{-1}$ , which is 5 times larger than the initial discharge capacity ( $20.3 \text{ mA g}^{-1}$ ). The extra charge capacity could be ascribed to the decomposition of  $\text{Li}_2\text{C}_2\text{O}_4$ . Assuming that the charge capacity provided by NCM is  $25 \text{ mA g}^{-1}$ , the decomposition percentage of re- $\text{Li}_2\text{C}_2\text{O}_4$  is 16.7%. And for (b), according to the theoretical compensation capacity provided by  $\text{Li}_2\text{C}_2\text{O}_4$  is  $27.6 \text{ mAh g}^{-1}$  (while the weight ratio of NCM and  $\text{Li}_2\text{C}_2\text{O}_4$  is 76 wt.% and 4wt.% in cathode electrode), the decomposition percentage of re- $\text{Li}_2\text{C}_2\text{O}_4$  is 32.5%.

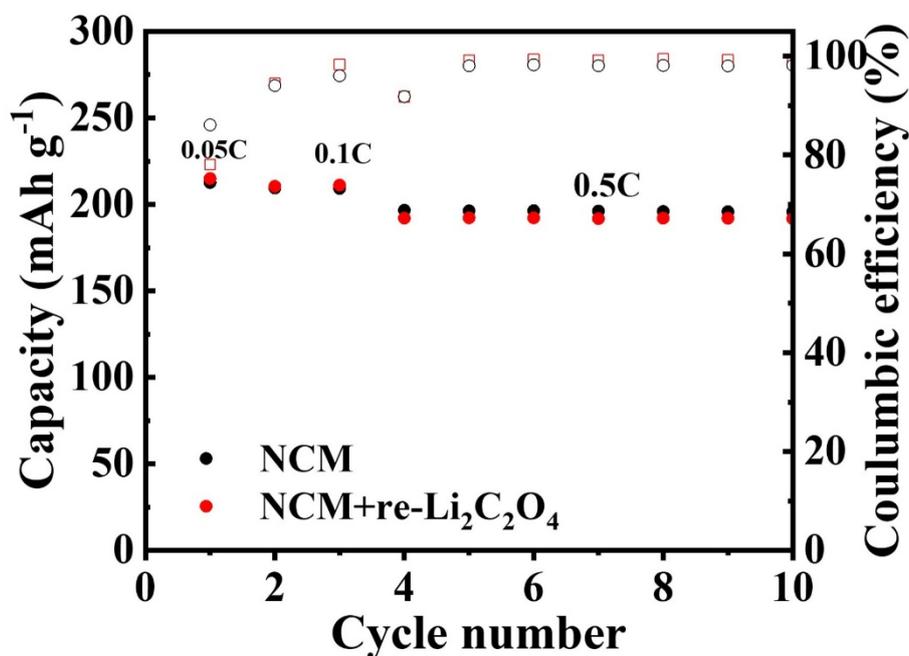


Figure S6 Electrochemical cycling performance of different electrode using NO electrolyte in half-cell. (1 C =  $200 \text{ mA g}^{-1}$ )

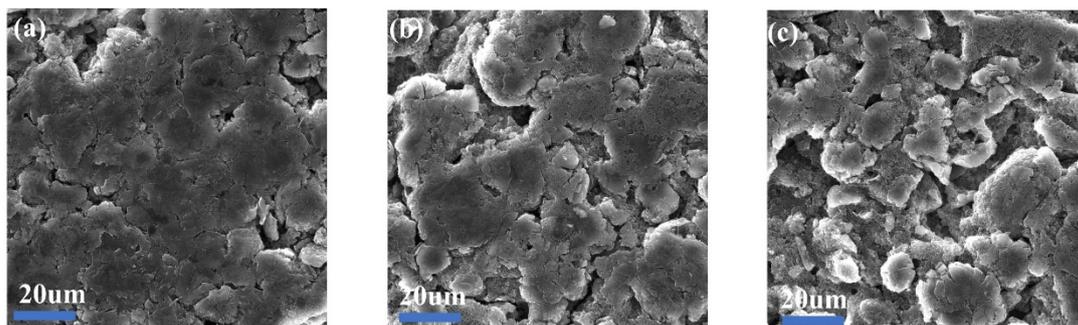


Figure S7 SEM images of Si-G (a) Pristine. (b) cycled in NO electrolyte. (c) cycled in baseline electrolyte.

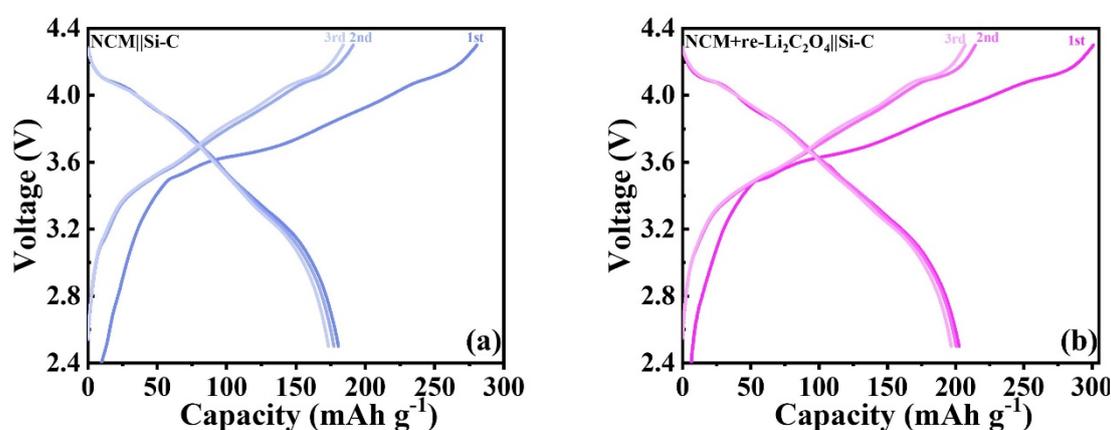


Figure S8 Initial three cycles of full cells. (a) NCM||Si-G, and (b) NCM(re-Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)||Si-G. The charge/discharge procedure for the initial 3 cycles is 0.05 C for the 1st cycle and 0.1 C for the following two cycles, where 1 C=200 mA g<sup>-1</sup>.

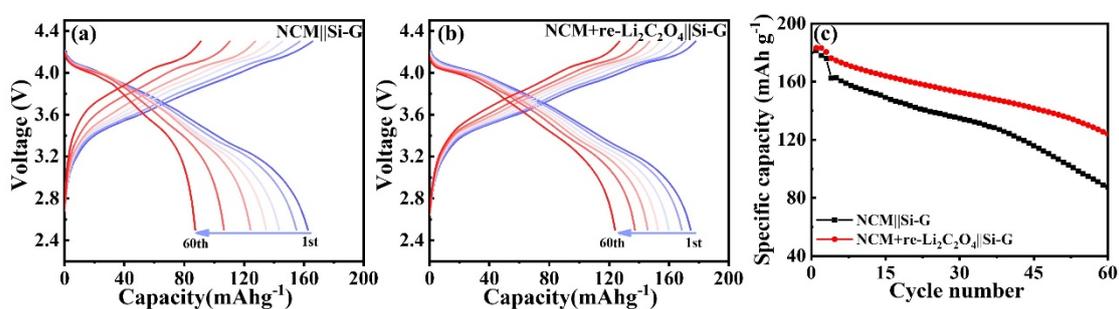


Figure S9 Electrochemical cycling performance of different electrodes using baseline electrolyte in full cells. Charge and discharge curves of the full cells. (a) NCM||Si-G and (b) NCM (re-Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)||Si-G. (c) The specific capacity of the NCM (re-Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)||Si-G and NCM||Si-G full-cells.

**Table S1. Comparison of the Electrochemical properties between our work and different pre-lithiation methods.**

Cathode	Prelithiation additive	Addition amount (wt%)	Charge Cut-off voltage (V)	Increased 1st charge capacity (mAh g <sup>-1</sup> )	Residue	Ref
LiNi <sub>0.83</sub> Co <sub>0.07</sub> Mn <sub>0.1</sub> O <sub>2</sub>	Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	4	4.3	28.4	No left	This work
LiCoO <sub>2</sub>	0.55Li <sub>2</sub> O: 0.45Li <sub>2/3-</sub> <sub>x</sub> Mn <sub>1/3</sub> O <sub>5/6</sub>	2	4.5	17.3	Unreacted Li <sub>2</sub> O	10
LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub>	Li <sub>2</sub> C <sub>4</sub> O <sub>4</sub>	2.5 5 10	4.5	2.7 18.1 32.7	Unreacted Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	11
LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub>	Fe/LiF/Li <sub>2</sub> O	4.8	4.4	31	Fe <sub>3</sub> O <sub>4</sub> & unreacted additives	12
LiCoO <sub>2</sub>	Mo <sub>2</sub> C/nano- Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	10	4.4	52	Mo <sub>2</sub> C	9
LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	Li <sub>2</sub> O <sub>2</sub>	2	4.6	28	1%NCM & impurities	13
LiCoO <sub>2</sub>	Li <sub>3</sub> N	2.5	4.5	51	Unreacted Li <sub>3</sub> N	14
Li <sub>1.15</sub> Ni <sub>0.17</sub> Co <sub>0.11</sub> Mn <sub>0.57</sub> O <sub>2</sub>	Li <sub>2</sub> O	3 6 9	4.8	8.2 24.6 5.3	Unreacted Li <sub>2</sub> O	15
LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>	Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.5 5	4.7	15 29	Unreacted Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5
LiCoO <sub>2</sub>	Li <sub>5</sub> FeO <sub>4</sub>	7	4.3	68	LiFeO <sub>2</sub>	16
LiFePO <sub>4</sub>	NiO/Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	20	4.5	107	NiO	7

## References

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