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Supplementary Materials

Deciphering the "Thermal Snap" on Ultra-High Ni Cathodes via Multi-Modal *Operando* Synchrotron X-ray and Mass Spectrometry

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1. Experimental Details

1.1. Sample Preparation

To verify the performance of the designed heating stage, charged polycrystalline NCM96 composite cathodes were employed as a model system. The cathode slurry was prepared by mixing NCM96 active material, carbon black, and polyvinylidene fluoride (PVDF) binder with a mass ratio of 8:1:1, and then coated onto a 10 μm ultrathin Al foil current collector with the loading of ~7 mg cm^{-2}. Electrochemical delithiation was carried out in CR2032 half cells assembled with lithium metal as the counter electrode, a glass fiber (GF) separator, and a commercial electrolyte consisting of ethylene carbonate/dimethyl carbonate (EC/DMC). The cells were charged to 4.3 V at 0.1 C, followed by a constant-voltage hold until the current decreased to 0.02 C, yielding a charge capacity above 240 mAh g^{-1}. Based on the theoretical capacity of NCM96, this corresponds to a nominal delithiation degree of approximately 87%. After charging, the cells were transferred into an Ar-filled glovebox and disassembled without air exposure. The charged composite electrodes were thoroughly rinsed with anhydrous DMC to remove free residual electrolyte, vacuum-dried, and then used for subsequent structural and gas-evolution measurements. Therefore, the heated samples contained NCM96 active material, carbon black, and PVDF binder, but no free electrolyte was intentionally retained during the thermal measurements. These similarly prepared charged composite electrodes were used separately for *operando* XRD, *operando* XAFS, and online mass spectrometry measurements.

1.2. Operando XRD Measurement

Operando XRD measurements were carried out using the developed heating stage on both a laboratory-based X-ray diffraction setup in our group and the BL02U2 beamline at the Shanghai Synchrotron Radiation Facility (SSRF). For the synchrotron XRD experiments, monochromatic X-rays with an energy of 17.7 keV were used, and the diffraction patterns were collected with a 2D flat-panel detector (Pilatus 2M). The charged NCM96 electrodes were mounted in the heating stage and measured under controlled heating conditions to track the structural evolution during thermal treatment. For the ramping measurements, the sample was heated from 25 to 550 °C at 5 °C min^{-1}.

1.3. Operando XAFS Measurement

Operando XAFS measurements at the Ni K-edge were performed at the ODE beamline of the SOLEIL synchrotron facility using the same heating stage. To ensure direct comparison with the operando XRD result, the sample configuration and heating protocol were kept as consistent as possible across different measurements. The

XAFS experiments were used to monitor the evolution of the Ni electronic state and local coordination environment of the charged NCM96 cathodes during heating.

1.4. OMS Measurement

Gas evolution during thermal treatment was monitored by online mass spectrometry using a HIDEN mass spectrometer. The heating stage was operated under a continuous flow of high-purity Ar, which served as the carrier gas to transport the released gaseous products from the chamber to the mass spectrometer. The gas-sampling line was connected through a Swagelok three-way fitting, into which the capillary inlet of the mass spectrometer was inserted for real-time signal acquisition. Both ramping and isothermal heating protocols were used in the gas-analysis experiments. For the ramping measurements, the sample was heated from 25 to 550 °C at 5 °C min^{-1}.

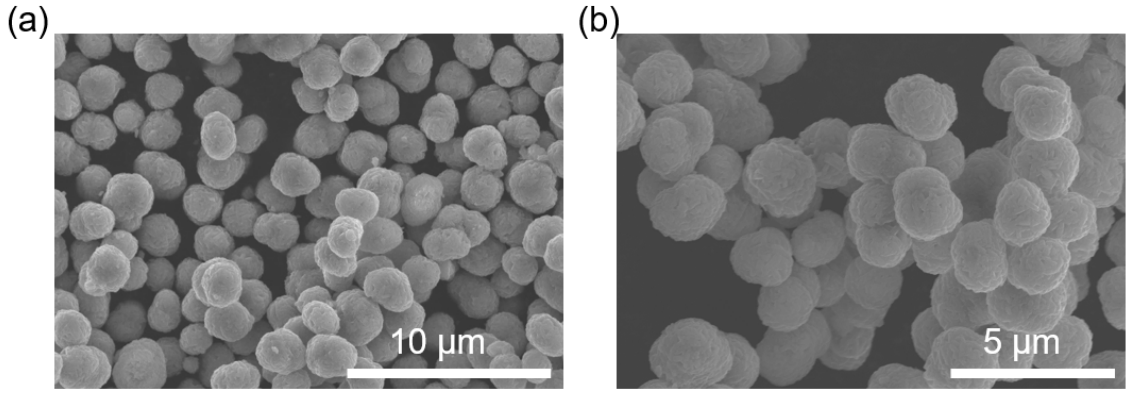

Figure S1. SEM images of pristine NCM96 powder: (**a**,**b**) images at different magnifications.

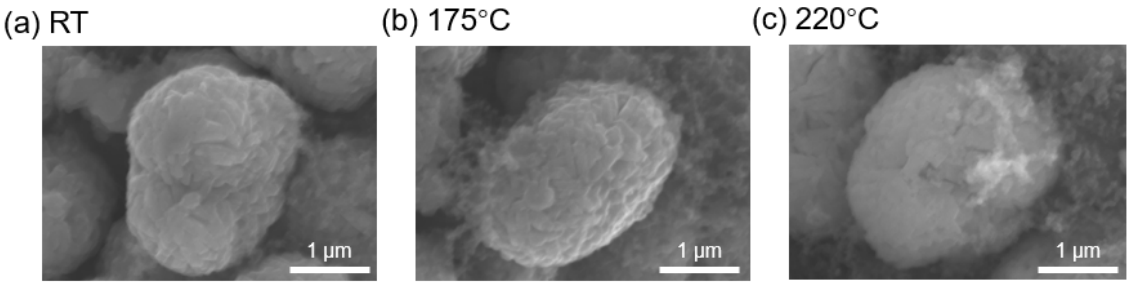

Figure S2. SEM images of delithiated NCM96 (charged to 4.3 V) at different temperatures: (**a**) room temperature; (**b**) 175 °C; and (**c**) 220 °C.

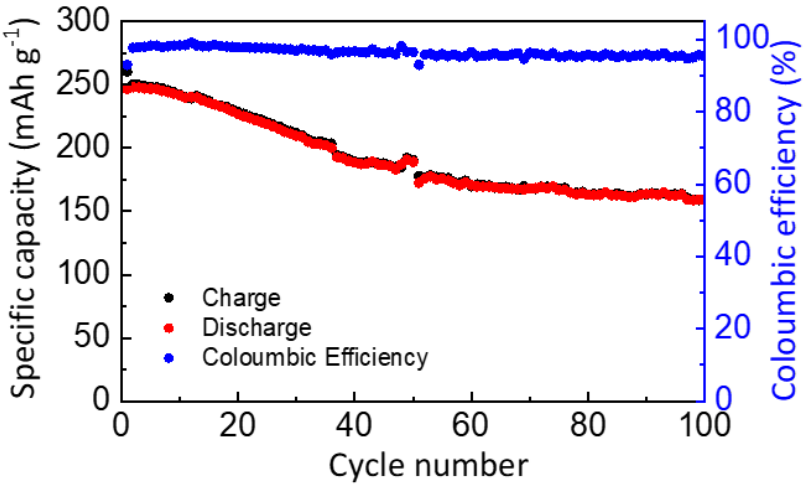

Figure S3. Long-term cycling performance of NCM96 measured at 0.1 C between 2.8 and 4.3 V for 100 cycles.

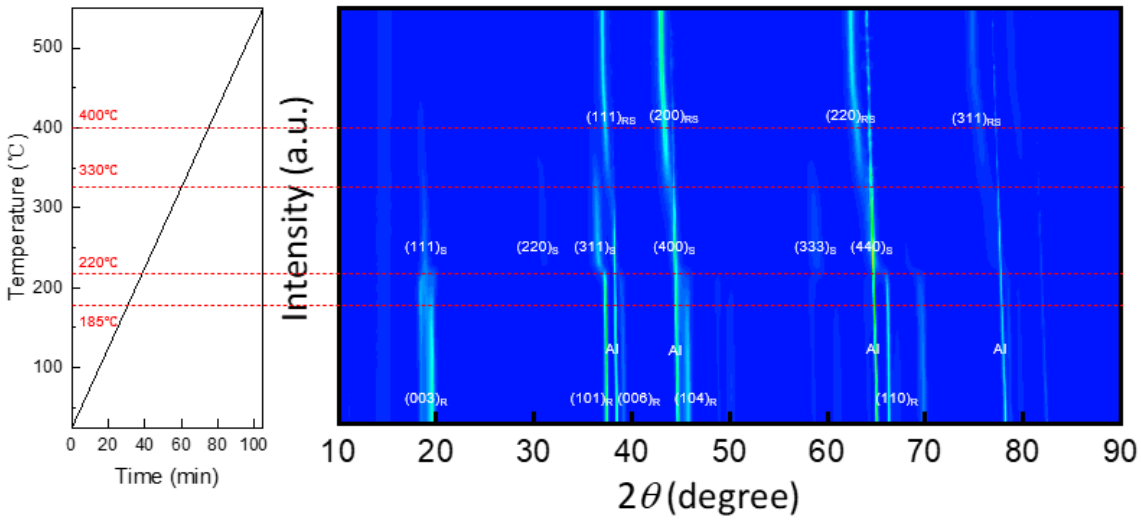

Figure S4. Full-pattern *operando* XRD evolution of delithiated NCM96 (Cu Kα equivalent, 10–90°) during heating from 25 to 550 °C at 5 °C min^{-1}. The dashed lines mark selected characteristic temperatures during thermal decomposition.

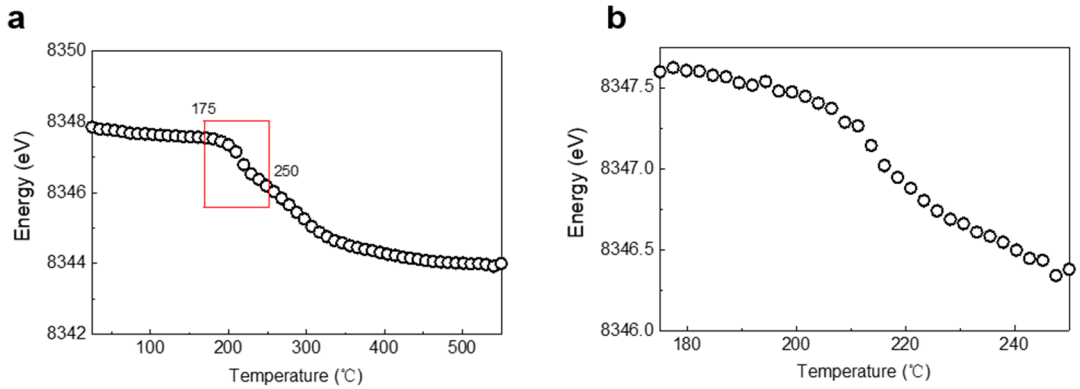

Figure S5. Reprocessed Ni K-edge evolution of delithiated NCM96 during heating. (**a**) Temperature-dependent Ni K-edge position extracted from the operando ED-XAFS spectra processed using 200-frame averaging. The red box highlights the critical temperature region from 175 to 250 °C. (**b**) Enlarged Ni K-edge position evolution in the 175–250 °C region reprocessed using 40-frame averaging.

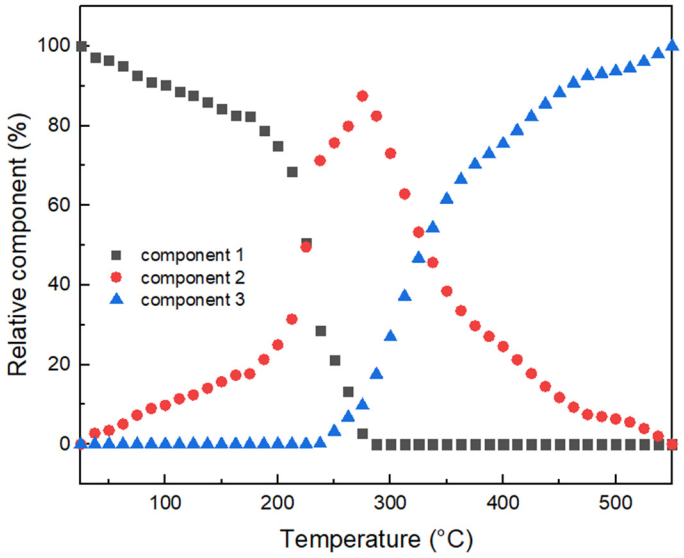

Figure S6. Temperature-dependent evolution of Ni K-edge XAFS components in delithiated NCM96 resolved by MCR-ALS: Component 1—initial charged state; Component 2—intermediate thermally evolved state; Component 3—final high-temperature state.

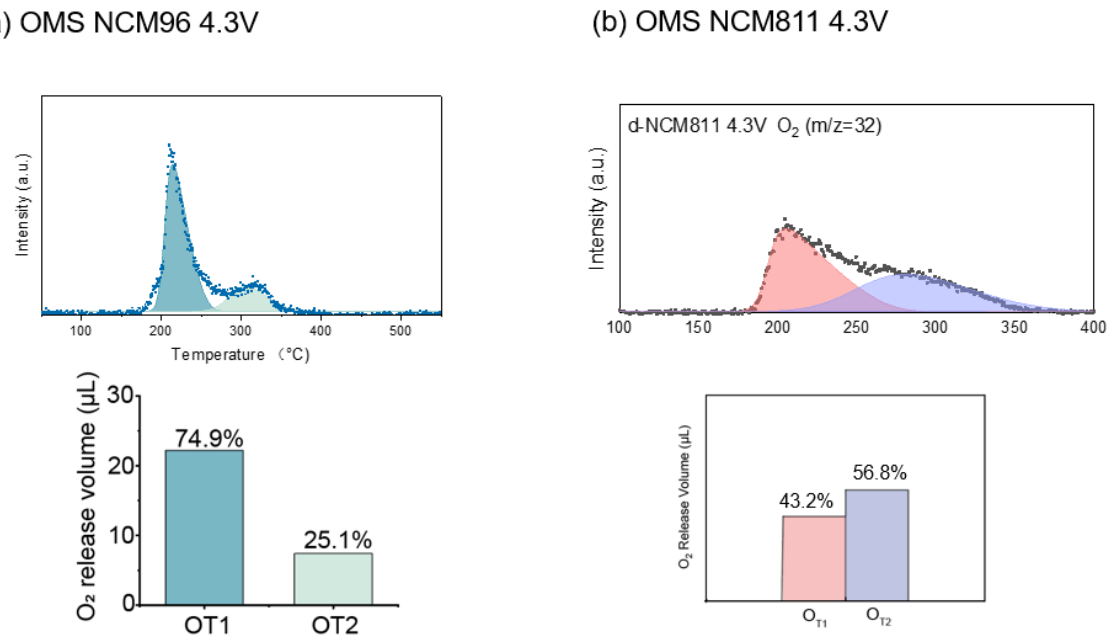

Figure S7. Comparison of O_2 evolution behavior between delithiated NCM96 and NCM811 at 4.3 V. (**a**) OMS profile and quantitative contribution of the two oxygen-release stages for NCM96; (**b**) Corresponding OMS result for NCM811 at 4.3 V, adapted from our previous work.