Supporting Information

Structural elucidation of degradation mechanism of nickel-rich layered cathodes during high-voltage cycling

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1. EXPERIMENTAL SECTION

1.1 Material preparation

1.1.1 Preparation of N85CM.

The precursor of N85CM is synthesis by sol-gel method. The detailed procedure has been reported before.[18-22] Stoichiometric amounts of $Ni(CH_3COO)_2 \cdot 4H_2O$ (98%, Chron Chem), $Co(CH_3COO)_2 \cdot 6H_2O$ (99.5%, Chron Chem), and $Mn(CH_3COO)_2 \cdot 4H_2O$ (99%, Chron Chem) were dissolved in citric acid monohydrate (99.5%, Chron Chem) solution to achieve Ni: Co: Mn molar ratio of 85:10:5, and the molar ratio of citric acid to total metal ions was 1:1. The mixture was stirred for 3 h at 30°C, then stirred at 95°C until a viscous gel was obtained. The resulting sol-gel material was vacuum-dried for 5 h at 120°C and subsequently heat to 500°C for 5 h under oxygen atmosphere to remove acetate and citric acid. The obtained precursor was ground with $LiOH \cdot H_2O$ (lithium excess 10%), and calcined at 500°C for 5 h and then at 780°C for 15 h under oxygen atmosphere.

1.1.2 Preparation of N85CMA.

To achieve citric acid solution with $Ni(CH_3COO)_2 \cdot 4H_2O$ (98%, Chron Chem), $Co(CH_3COO)_2 \cdot 6H_2O$ (99.5%, Chron Chem), $Mn(CH_3COO)_2 \cdot 4H_2O$ (99%, Chron Chem) and $Al(CH_3COO)_3 \cdot 18H_2O$ (99%, Chron Chem) at a molar ratio of 85:10:3:2. Then the followed steps are the same as described above. For comparison, the traditional $LiCoO_2$ cathode was also prepared by high-temperature solid-state reaction.

1.2. Material Characterization

The crystalline structural evolution of N85CM and N85CMA was characterized by high-resolution synchrotron radiation diffraction (SRD). *In situ* SRD experiments were performed at the beamline MSPD at ALBA (Barcelona, Spain), using synchrotron radiation with an energy of 30 keV (λ = 0.41287 Å) and an exposure time of 60 seconds per pattern. The diffraction patterns were collected using a MYTHEN 1D position sensitive detector. For *in-situ* diffraction measurements, CR2025 coin cells with glass windows (diameter = 5 mm) were used. The unit cell parameters of N85CM and N85CMA were refined to the SRD patterns using Fullprof software. The refinements were performed by using a single α-$NaFeO_2$ layered structure model where Li ions and transition metals (TMs) are positioned on 3*b* site and 3*a* site, respectively, and oxygen ions are situated on 6*c* site. Then, the structures of N85CM and N85CMA cathodes were refined precisely against SRD

diffraction data with a single structural model with constrained structural parameters. Particle morphology and structure were measured by scanning electron microscopy (SEM, Hitachi, S-4800). The element mapping is performed by energy dispersive spectroscopy (EDS) using the same instrument with the SEM characterization. The cross-sectional SEM images were detected by FIB (HELIOS NanoLab 600i, FEI, USA).

1.3. Electrochemical measurements

The positive electrode of the battery is composed of 80 wt.% positive electrode material, 13 wt.% acetylene black, 7 wt.% PVDF (polyvinylidene fluoride), and moderate amount of NMP (N-methyl-2-pyrrolidone). The mixture was ball milled for 16 minutes and then spread into a uniform film on an Al foil, subsequently vacuum-dried for 12 h at 120°C to remove NMP. The loading mass of the positive material in the electrode was 4 ± 0.5 mg cm^{-2}. The coin cells were assembled with positive electrode, separator (Celgard 2400), lithium plate and electrolyte (1M LiPF$_6$ dissolved in ethylene carbonate and dimethyl carbonate (1:1vol)) using CR2025 cases in glove box. The coin cells were tested at a current density of 0.1 C (1 C = 270 mA·g^{-1}) between 2.7 and 4.8 V (versus Li/Li$^+$).

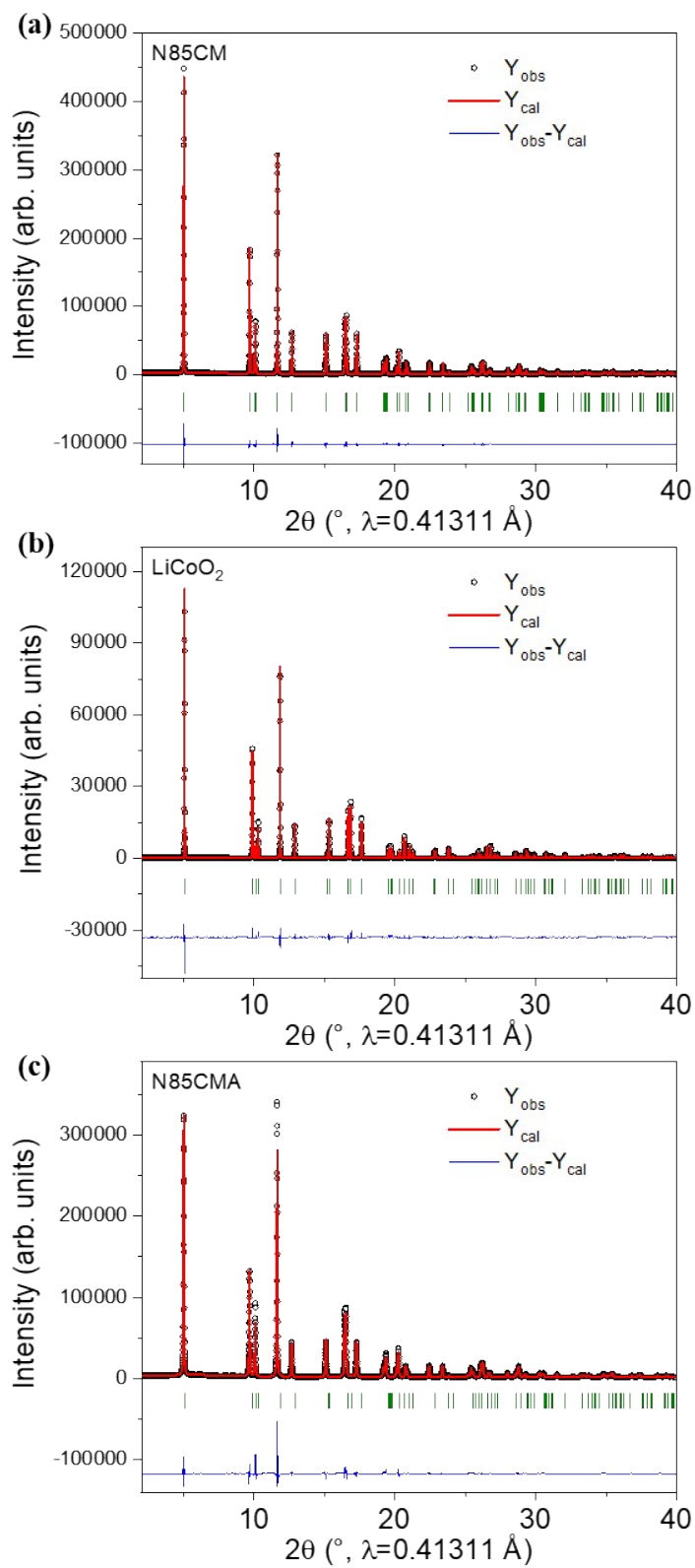## 2. Additional results and discussion

Figure S1. Rietveld refinement against SRD patterns of (a) N85CM, (b) LiCoO₂ and (c) N85CMA.
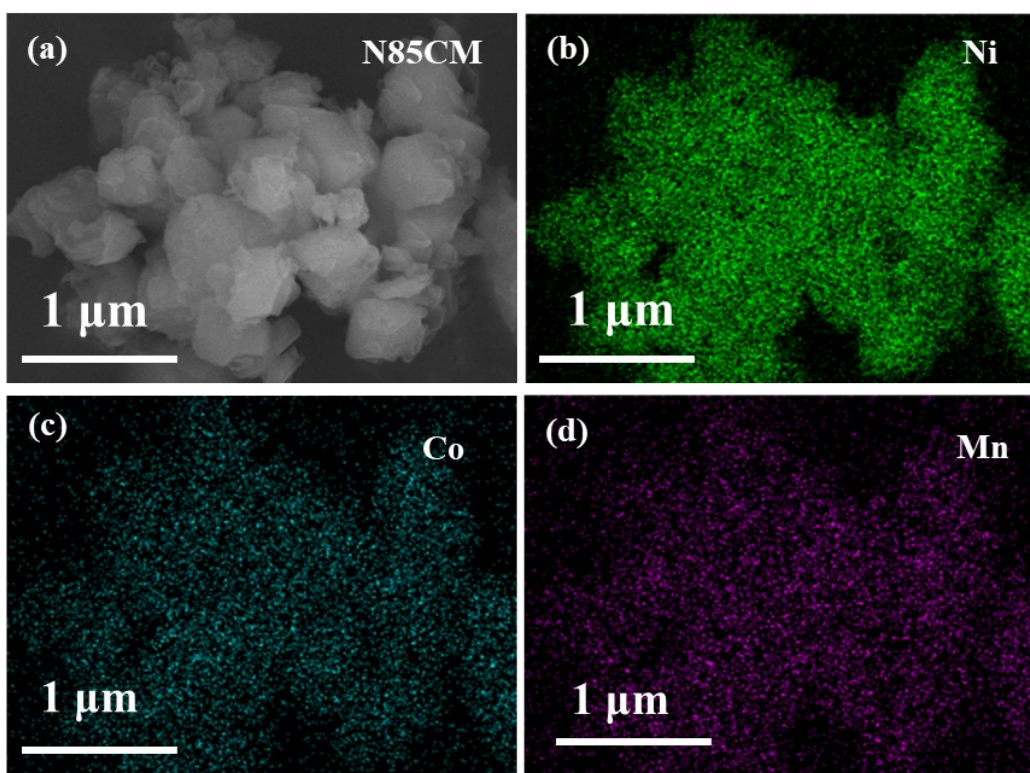
Figure S2. (a) SEM image and (b-d) EDS mappings of N85CM.

The SEM images of the as-prepared N85CM cathode material (Fig. S2a) exhibit that the secondary particles are formed by agglomeration of primary particles, and the EDS mappings (Fig. S2b, c and d) reveal the uniform distributions of TMs.
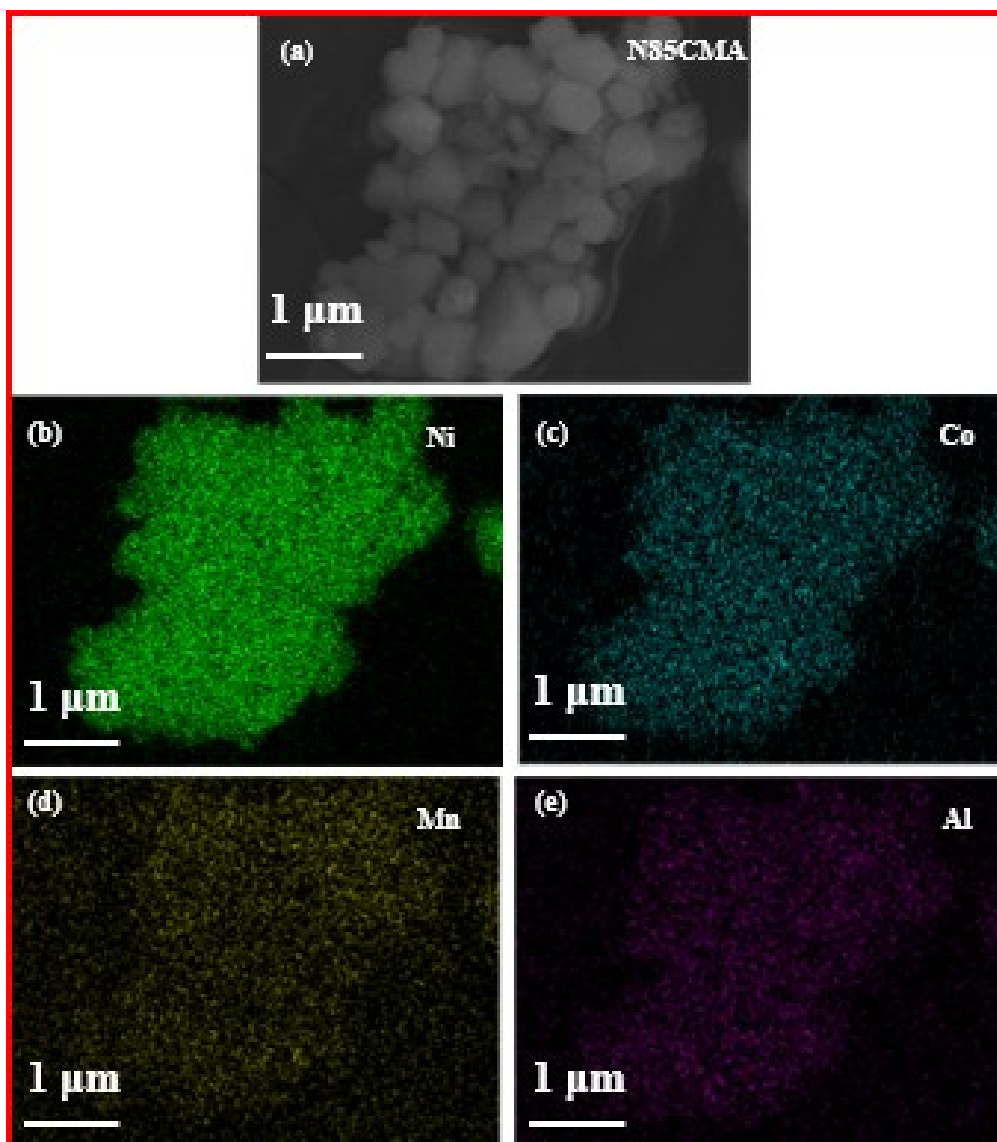
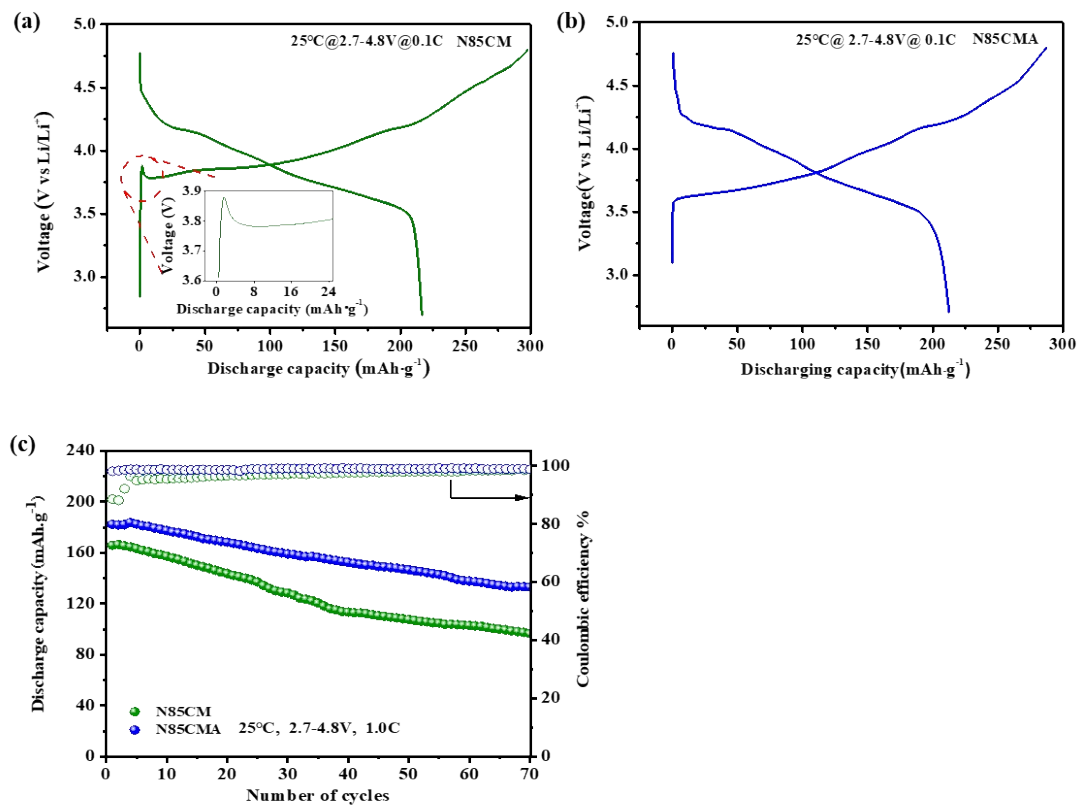Figure S3. (a) SEM image and (b-e) EDS mappings of N85CMA.

Figure S4. Voltage profiles for first cycle of (a) N85CM and (b) at a voltage range of 2.7-4.8 V. Cycling performances of N85CM and N85CMA with voltage range of 2.7-4.8V at 1.0 C and 25℃ are also shown in (c).
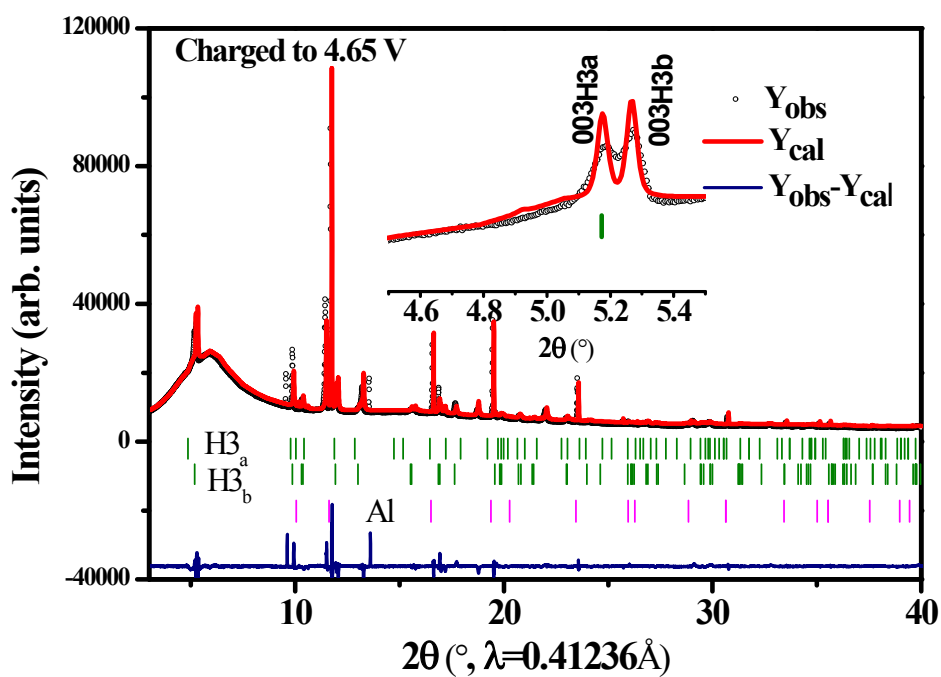
Figure S5. Rietveld refinement results of H3$_a$-H3$_b$ biphasic region at 4.65 V of N85CM are exhibited in Figure 1(a-b).
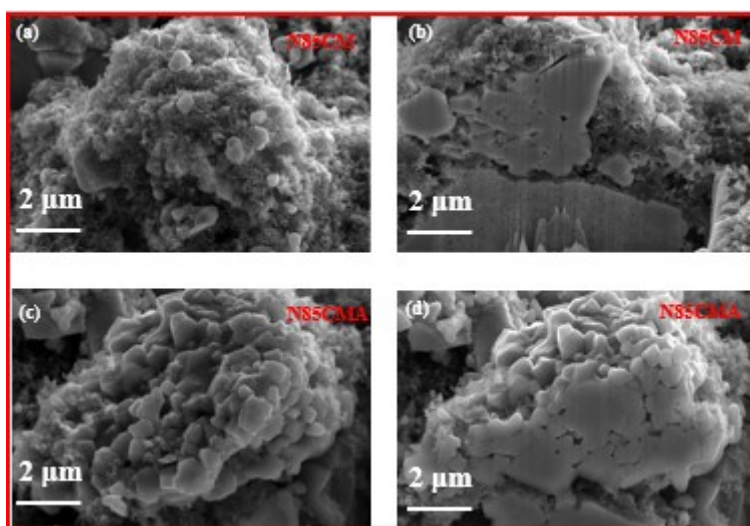

Figure S6. SEM image of (a) N85CM and (c) N85CMA after cycles. Cross-section images of the fully discharged cathodes after 100 cycles: (b) N85CM and (d) N85CMA.