

## Supporting Information

# Capacity Fading of Ni-Rich NCA Cathodes: Effect of Microcracking Extent

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## EXPERIMENTAL METHODS

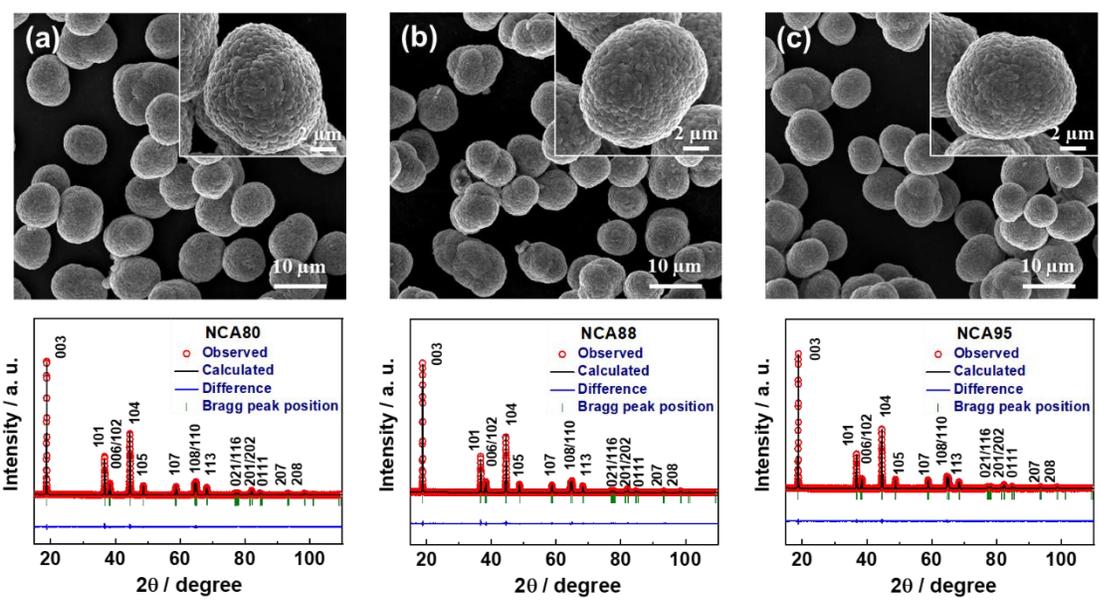
*Synthesis of Li[Ni<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>]O<sub>2</sub> cathodes:* Precursors of NCA 80, NCA 88, NCA 95, and LNO (i.e., [Ni<sub>0.83</sub>Co<sub>0.17</sub>](OH)<sub>2</sub>, [Ni<sub>0.90</sub>Co<sub>0.10</sub>](OH)<sub>2</sub>, [Ni<sub>0.96</sub>Co<sub>0.04</sub>](OH)<sub>2</sub>, and Ni(OH)<sub>2</sub>, respectively) were prepared by co-precipitation method. Synthesis was conducted by using a metal sulfate solution corresponding to the composition of each precursor. First, 2 mol L<sup>-1</sup> of metal sulfate solution was prepared by dissolving NiSO<sub>4</sub> • 6H<sub>2</sub>O and CoSO<sub>4</sub> • 7H<sub>2</sub>O (Samchun Chemical, Korea) in deionized water (Ni:Co ratio is 83:17 for NCA 80, 90:10 for NCA 88, 96:4 for NCA 95, and 100:0 for LNO in molar ratio, respectively). Then, Metal sulfate solution was pumped into a 17 L batch reactor containing NaOH (aq., Samchun Chemical, Korea) and NH<sub>4</sub>OH (aq., Junsei, Japan). Simultaneously, 4 mol L<sup>-1</sup> of NaOH (aq.) was pumped into the reactor to maintain pH, and 10.5 mol L<sup>-1</sup> of NH<sub>4</sub>OH (aq.) was pumped as chelating agent. N<sub>2</sub> gas was fed continuously into the reactor to prevent oxidation reaction during synthesis. After 24 h of reaction, the synthesized precursors were washed, filter pressed, and dried for 24 h in an oven at 110 °C. Hydroxide precursors were mixed with LiOH • H<sub>2</sub>O and Al(OH)<sub>3</sub>, respectively, according to molar ratio (Li:transition metal:Al = 1.01:0.96:0.04 for NCA80, 1.01:0.98:0.02 for NCA 88, 1.01:0.99:0.01 for NCA95, and 1.01:1:0 for LNO), and the mixtures were calcined 750 °C, 730 °C, 700 °C, and 650 °C respectively, to obtain stoichiometric Li[Ni<sub>0.8</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>]O<sub>2</sub>, Li[Ni<sub>0.88</sub>Co<sub>0.10</sub>Al<sub>0.02</sub>]O<sub>2</sub>, Li[Ni<sub>0.95</sub>Co<sub>0.04</sub>Al<sub>0.01</sub>]O<sub>2</sub>, and LiNiO<sub>2</sub>.

*Characterization of materials:* The chemical composition of materials was confirmed by ICP (iCAP 7000 SERIES, Thermo Fisher Scient). The morphology and cross-sectional image of materials was analyzed by SEM (Verios G4UC, FEI). To polish the cross-section of materials, the cathode electrodes were prepared by disassembling cells charged/discharged at various voltage, washing with dimethyl carbonate, and drying in an Ar-filled glove box. The cross-section of those electrodes were polished by the Cross-section Polisher (JEOL SM-09010, JEOL). All cross-sectional SEM image was analyzed by using 'Adobe

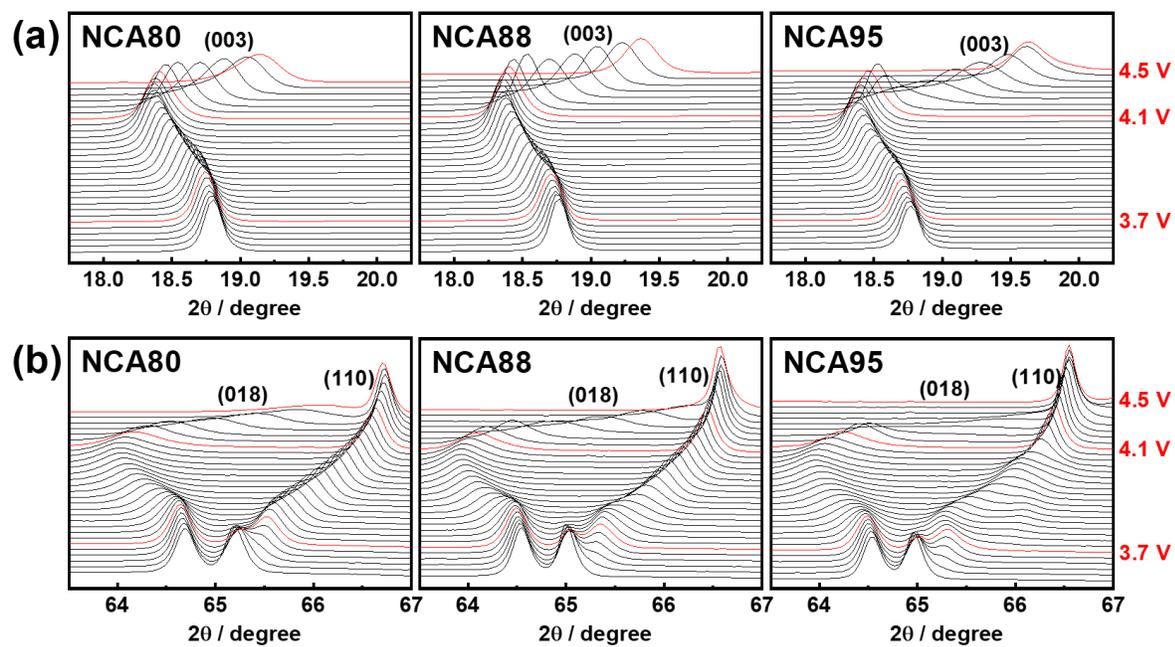
Photoshop' and 'Image J' software programs. After obtaining the cross-sectional SEM images of secondary particle, the boundary of grains and microcracks was selected. Inside of the border line of particles are colored into two different types; one containing only grains except the microcracks, and the other including both grains and microcracks. Two kind of images are converted into 8-bit images, and the pixels, which is colored in previous step, are extracted and counted by Image J software program. The ratio of counted pixels between two image is calculated areal fraction of microcracks. The crystalline phase was analyzed by XRD (Empyrean, Panalytical) in the  $2\theta$  range of  $10\text{--}130^\circ$  with  $0.02^\circ$  step size using  $\text{Cu K}\alpha$  radiation. The details of crystal structure were analyzed by Rietveld refinement using FullProf suite. In-situ XRD investigations of the structural changes were conducted with the 6D-UNIST beamline at the Pohang Accelerator Laboratory (PAL) in Pohang, Korea. The wavelength ( $\lambda$ ) from the synchrotron radiation was  $0.65303 \text{ \AA}$ , and a beam calibration to fit the distance of sample-to-detector was performed by using the  $\text{CeO}_2$  standard. While the modified 2032 coin-type half-cell with a Kapton window was charged with a constant current of 40 mA, XRD patterns were acquired every 4 min simultaneously with a 2D charge-coupled device detector (Rayonix MX225-HS) in transmission mode. The thermal stability of materials was examined by Differential scanning calorimetry (DSC 214 polyna, NETZSCH). To measure DSC, cathode electrodes were prepared by disassembling 2032 coin-type half-cells charged to 4.3 V. The electrodes are washed with dimethyl carbonate and dried in an Ar-filled glovebox. From the charged electrode, 7mg of the cathode material was taken by scratching the surface of electrode and loaded in high-pressure sample crucible with 100  $\mu\text{L}$  of electrolyte. The samples were analyzed with scan rate was  $5 \text{ }^\circ\text{C min}^{-1}$ .

*Electrochemical characterization:* To fabricate positive electrodes, the synthesized powder was mixed with Super-P, KS-6, and poly(vinylidene fluoride) (90 : 2.2 : 3.3 : 4.5 in weight ratio) in N-methylpyrrolidone with Thinky paste mixer (ARE-310, THINKY Corporation). The obtained slurry was coated onto Al foil with doctor blade, roll-pressed in 4 kN, and vacuum dried in 5 hours. Half-cell test

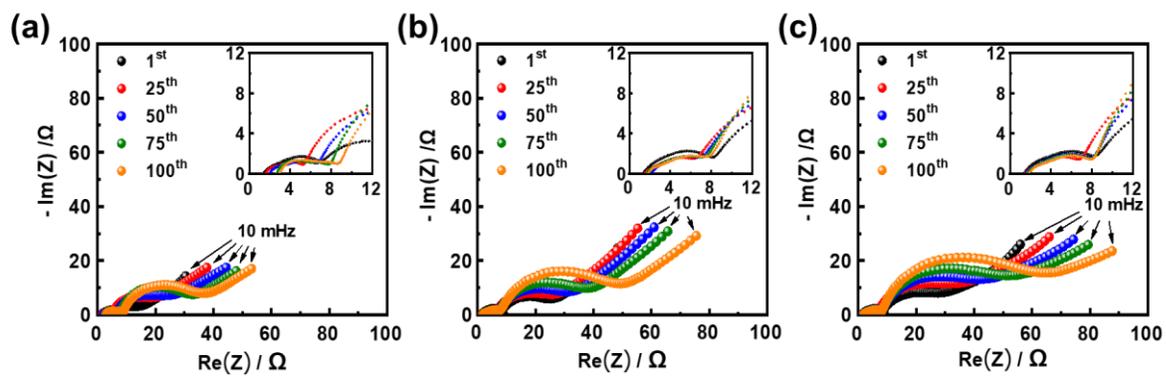
was carried out with 2032 coin-type half-cell composed of cathode, Li metal anode, separator (Celgard 2320, Celgard), and electrolyte (1.2 M LiPF<sub>6</sub> in ethylene carbonate : ethyl methyl carbonate (EC : EMC, 3 : 7 by vol%) with 2 wt% vinylene carbonate). A constant current density of 100 mA g<sup>-1</sup> (0.5 C-rate) was applied to the half-cells at 30 °C between 2.7 and 4.3 V by using battery-testing system (TOSCAT-3100U, Toyo System). Cyclic voltammetry was performed with scan rate of 0.22 mV s<sup>-1</sup> between 2.7 and 4.3 V and EIS was carried out in the frequency range of 1 mHz to 1 MHz with amplitude of 10 mV<sub>rms</sub> by using a multichannel potentiostat (VMP3, Bio-Logic). The pouch-type full-cells wrapped with an Al pouch were used to test long-term cycling performance. The anode was mesocarbon microbead graphite (MCMB, Osaka Gas) coated Cu foil and the electrolyte solution was same with the half-cell test. The cells were tested at 25 °C between 3.0 and 4.2 V by applying a constant 1 C current (35 mA corresponds to 200 mA g<sup>-1</sup>).



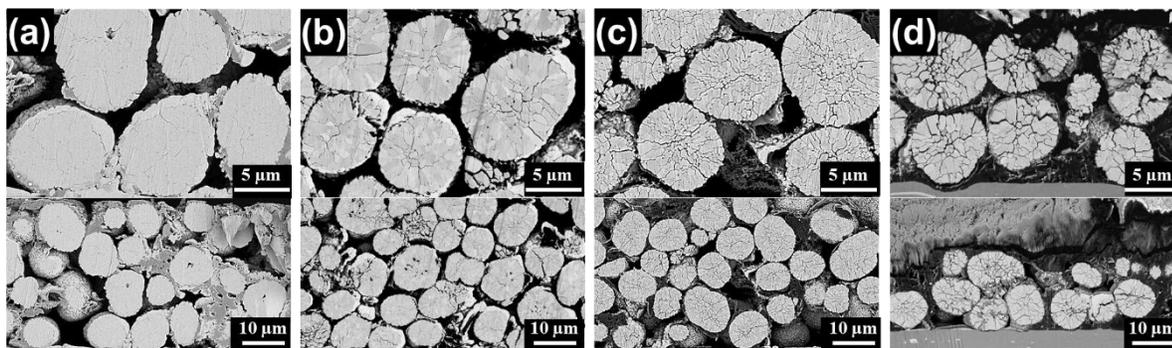
**Figure S1.** SEM images of lithiated oxide and results of Rietveld refinement for the a) NCA80, b) NCA88, and c) NCA95 cathodes.



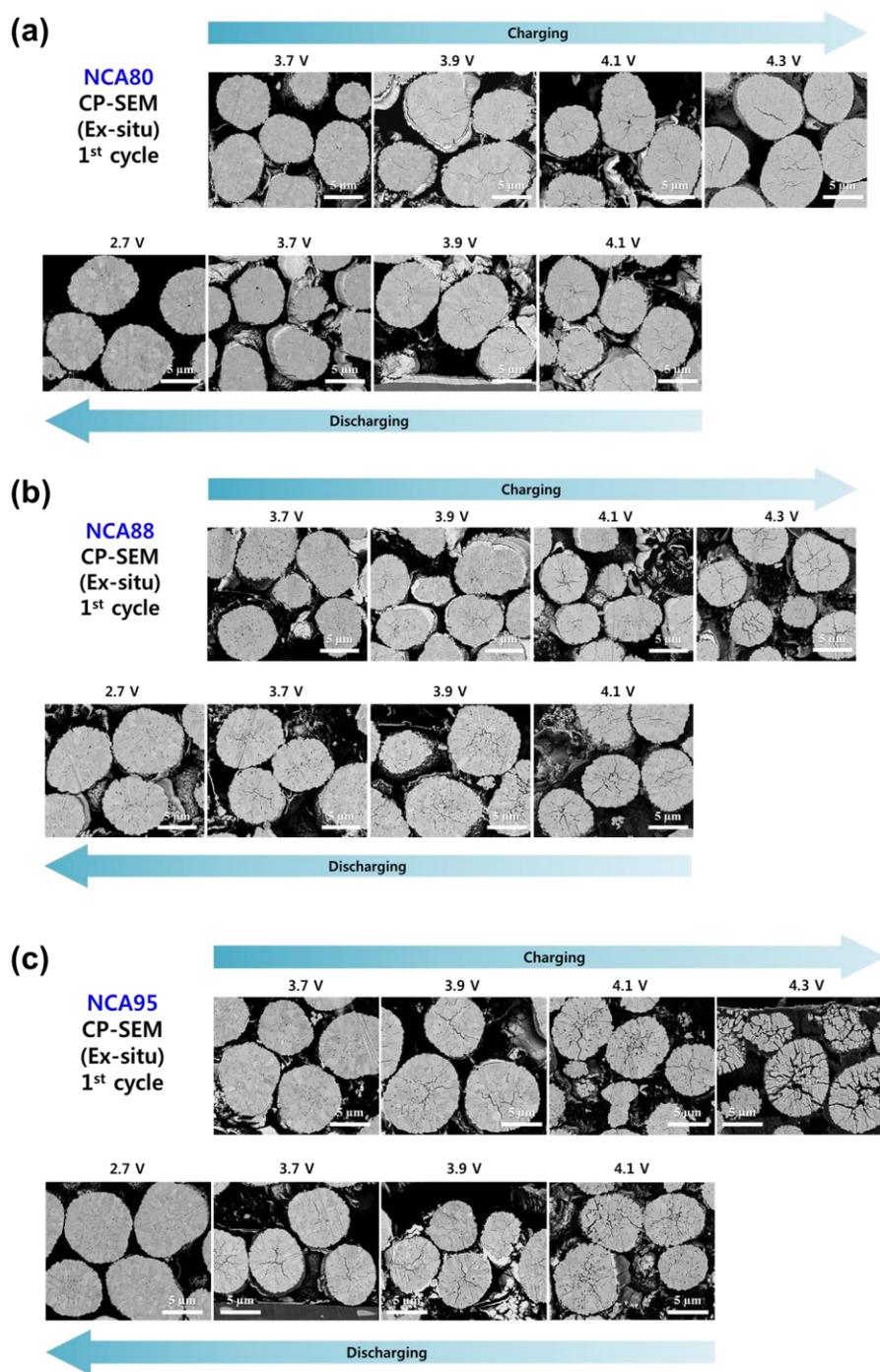
**Figure S2.** In situ XRD patterns showing the selected  $2\theta$  ranges of a) (003) and b) (110) reflections for the NCA80, NCA88, and NCA95 cathodes during initial charging to 4.3 V.



**Figure S3.** Nyquist plots of electrochemical impedance measured every 25 cycles for the a) NCA80, b) NCA88, and c) NCA95 cathodes.



**Figure S4.** Cross-sectional SEM images of cycled electrodes of a) NCA80, b) NCA89, c) NCA95, and d) LNO cathodes after 100 cycles using the half-cell.



**Figure S5.** Cross-sectional SEM images of charged/discharged electrodes of a) NCA80, b) NCA89, c) NCA95 cathodes in 1<sup>st</sup> cycle using the half-cell.

**Table S1.** Structural parameters determined by Rietveld refinement of the X-ray diffraction data for NCA powders.

<b>Material</b>	<b>a<sub>hex</sub> [Å]</b>	<b>c<sub>hex</sub> [Å]</b>	<b>V [Å<sup>3</sup>]</b>	<b>Cation mixing [%]</b>	<b>R<sub>p</sub></b>	<b>R<sub>wp</sub></b>	<b>χ<sup>2</sup></b>
<b>NCA80</b>	2.8641 (1)	14.1720 (1)	100.675 (2)	0.8	1.12	1.53	1.89
<b>NCA88</b>	2.8698 (1)	14.1843 (2)	101.164 (2)	1.2	1.83	2.48	2.08
<b>NCA95</b>	2.8726 (1)	14.1896 (1)	101.402 (1)	1.7	2.44	3.49	1.71

**Table S2.** Chemical composition of NCA80, NCA88, NCA95 and LNO identified by ICP-OES.

<b>Sample</b>	<b>Chemical composition</b>		
	<b>Ni (At %)</b>	<b>Co (At %)</b>	<b>Al (At %)</b>
<b>NCA80</b>	79.6	16.4	4.0
<b>NCA88</b>	87.7	10.3	2.0
<b>NCA95</b>	94.8	4.2	1.0
<b>LNO</b>	100.0		