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Supporting Information

Probing the Microstructural Changes in Li-Rich Layered Oxides Induced by Over-lithiation

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S1 Experimental Section

S1.1 Material Preparation

The lithium-rich manganese-based cathode material $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ (LLNMO) was synthesized by high-temperature solid-state method. The precursor of $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ was prepared using hydroxide co-precipitation method. A 2 M aqueous solution containing $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ with a ratio of 1:3 was continuously fed into the reactor. Concurrently, 4 M NaOH precipitation solution and controlled volumes of $NH_3 \cdot H_2O$ solution (chelating agent) were pumped into the reactor. Throughout the coprecipitation process, the pH value (11.0 ± 0.2), temperature (52 ± 2 °C), and stirring speed (600 rpm) were rigorously maintained. The entire reaction was performed under nitrogen atmosphere. The resulting precipitate was filtered, washed thoroughly, and dried at 80 °C for 12 h to obtain precursor powders. The prepared precursor was then homogeneously mixed with stoichiometric $LiOH \cdot H_2O$ (the molar ratio of Li:TM=1.05:1). Final $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ samples were synthesized by pre-calcination at 500 °C for 6 h followed by calcination at 900 °C for 12 h in air.

S1.2 Electrochemical Characterization

The electrochemical performance of LLNMO cathode was evaluated via galvanostatic cycling in CR2032 coin-type half-cells. The active LLNMO material, super P conductive agent and polyvinylidene fluoride (PVDF) were mixed at a mass ratio of 80 wt% :10 wt% :10 wt%. The slurry was prepared using NMP as the solvent and then coated on the Al foil followed by drying in a vacuum oven at 80 ℃ overnight. The cathode was cut into 12 mm diameter discs with the active material mass loading of approximately 3-4 mg cm^{-2}. Lithium metal was used as the anode, Celgard 2325 film as the separator, $LiPF_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC) 1:1 (v/v) (LP30) as the electrolyte. Cell assembly was performed in an argon-filled glove box (O_2/H_2O < 0.1 ppm). Galvanostatic charge-discharge tests were conducted at a Neware potentiostat, with a current density of 28 mA g^{-1} between 2.0 - 4.8 V and 1.0 - 4.8 V (*vs*. Li^+/Li) at 25 °C, respectively.

S1.3 Synchrotron X-ray Diffraction (sXRD)

To investigate the crystal structure evolutions of LLNMO cathode, *in situ* sXRD

experiment was performed at the beamline P02.1 of PETRA-III using synchrotron radiation with an energy of 60 keV (λ = 0.2072 Å) at ALBA synchrotron, Barcelona, Spain. The exposure time is 60 s per sXRD pattern. *In situ* electrochemical cells featuring beryllium X-ray transmission windows were employed to maintain electrochemical stability while enabling X-ray penetration. Two-dimensional (2D) diffraction patterns were acquired utilizing a 2D flat-panel detector (PerkinElmer amorphous-silicon detector) at the P02.1 beamline, with the distance between the sample and the detector maintained at approximately 1600 mm. Subsequently, the acquired 2D diffraction images were converted into one-dimensional (1D) diffraction patterns via the X-ray image processing software Fit2D. The sXRD data were collected at 0.1 C under over-discharge (1.0-4.8 V) condition. The crystallographic parameters and microstrain were obtained by the Rietveld method using the FULLPROF program.

S1.4 Material characterization

The micromorphology and elemental distribution of the sample were examined using a scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDS, MAIA3 LMH). Additionally, the quantitative chemical composition of LLNMO cathode was determined by inductively coupled plasma mass spectrometry (NexION 350D ICP-MS).

S2 Additional results

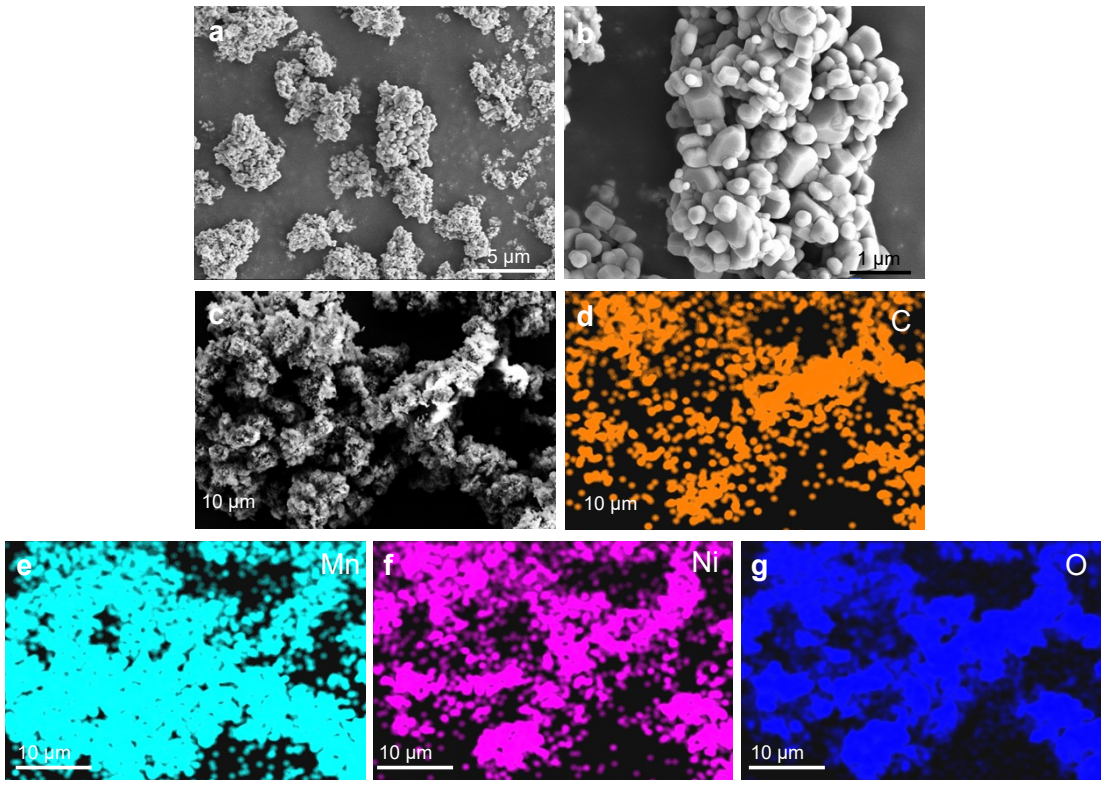

Figure S1. SEM and EDS mapping images of LLNMO.

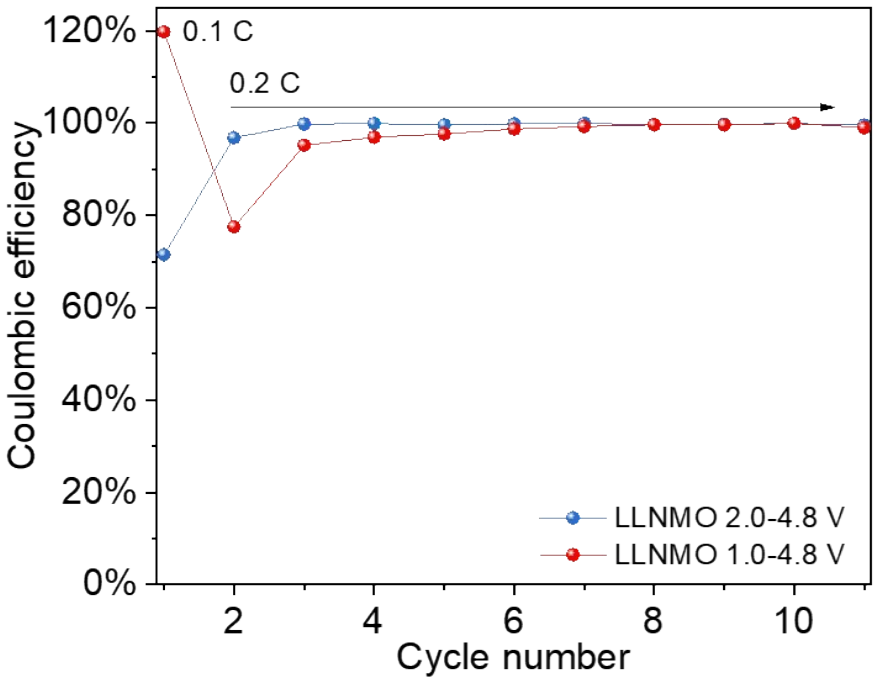

Figure S2. Coulombic efficiencies of LLNMO cathode within the voltage ranges of 2.0-4.8 and 1.0-4.8 V, respectively.

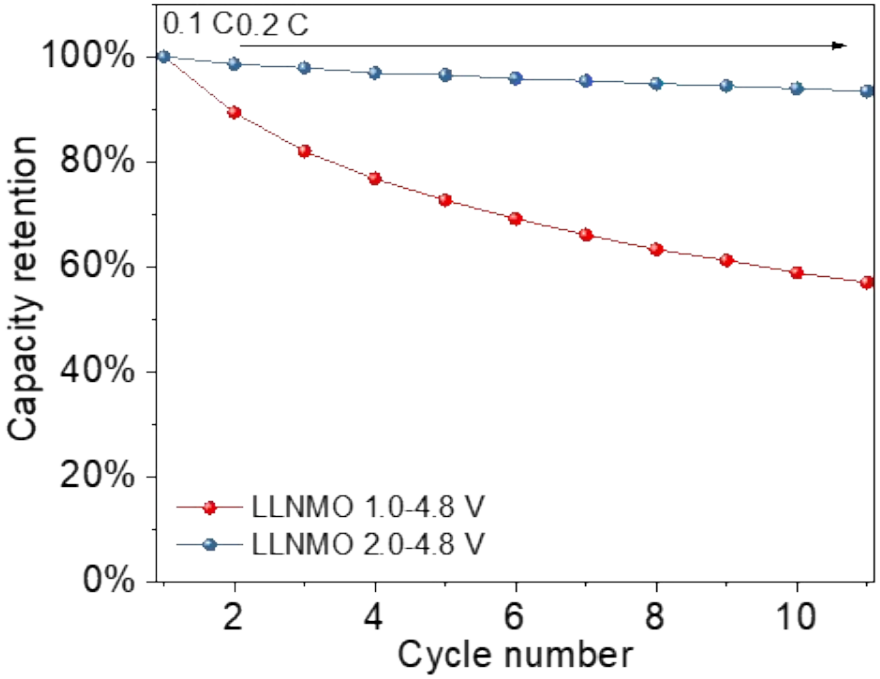

Figure S3. Capacity retention of LLNMO cathode within the voltage ranges of 2.0-4.8 V and 1.0-4.8 V, respectively.

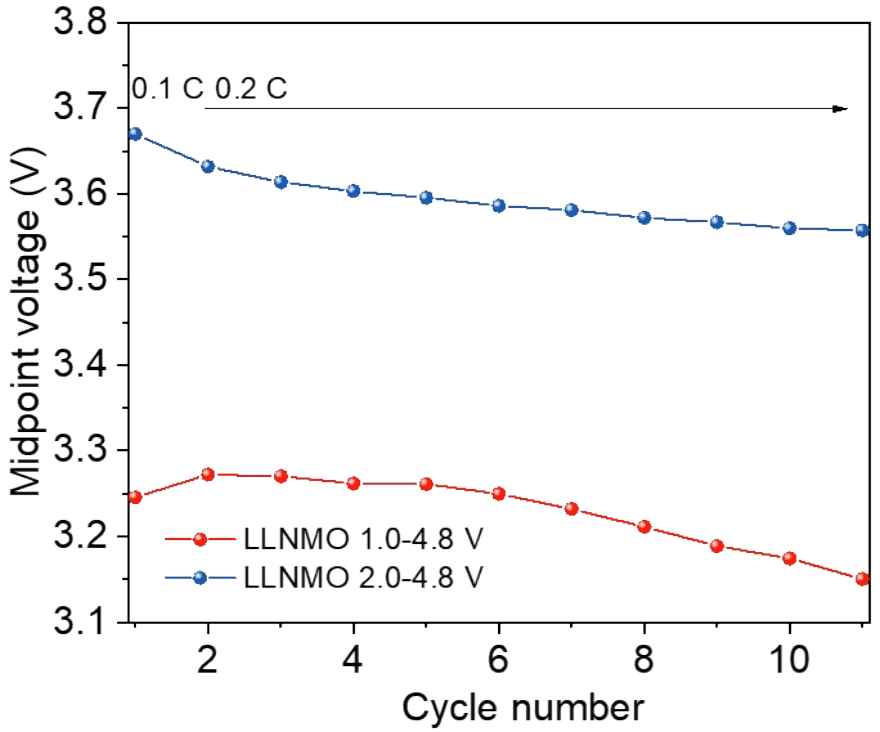

Figure S4. Voltage stability of LLNMO cathode within the voltage ranges of 2.0-4.8 V and 1.0-4.8 V, respectively.

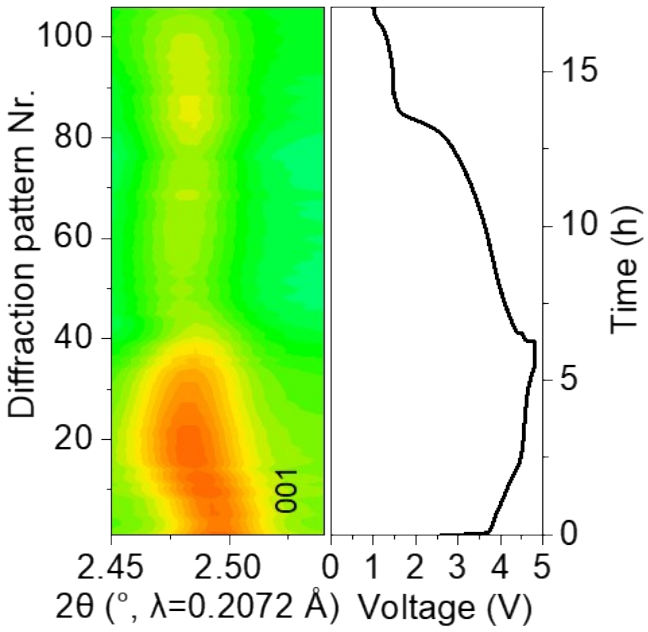

Figure S5. *In situ* sXRD patterns of LLNMO cathode at 0.1 C within a voltage range from 1.0 to 4.8 V.

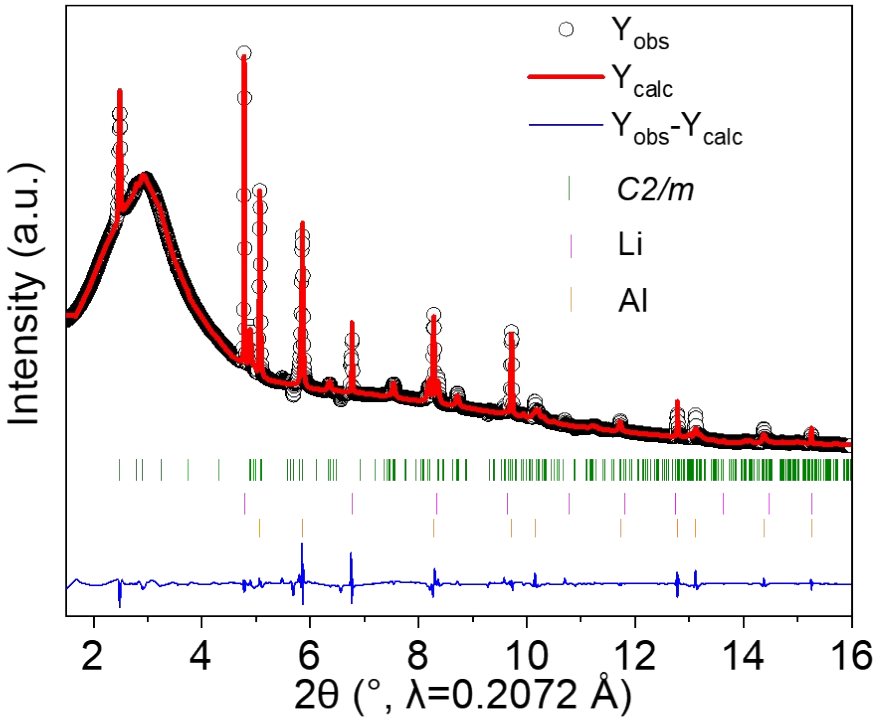

Figure S6. Rietveld refinement against sXRD pattern of LLNMO cathode charged to 4.5 V.

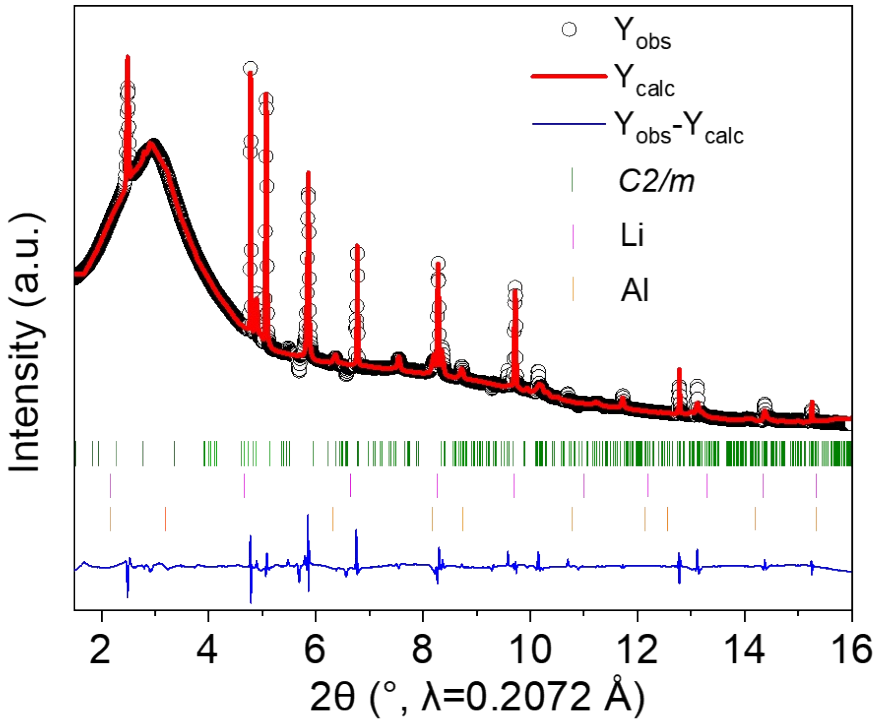

Figure S7. Rietveld refinement against sXRD pattern of LLNMO cathode charged to 4.8 V.

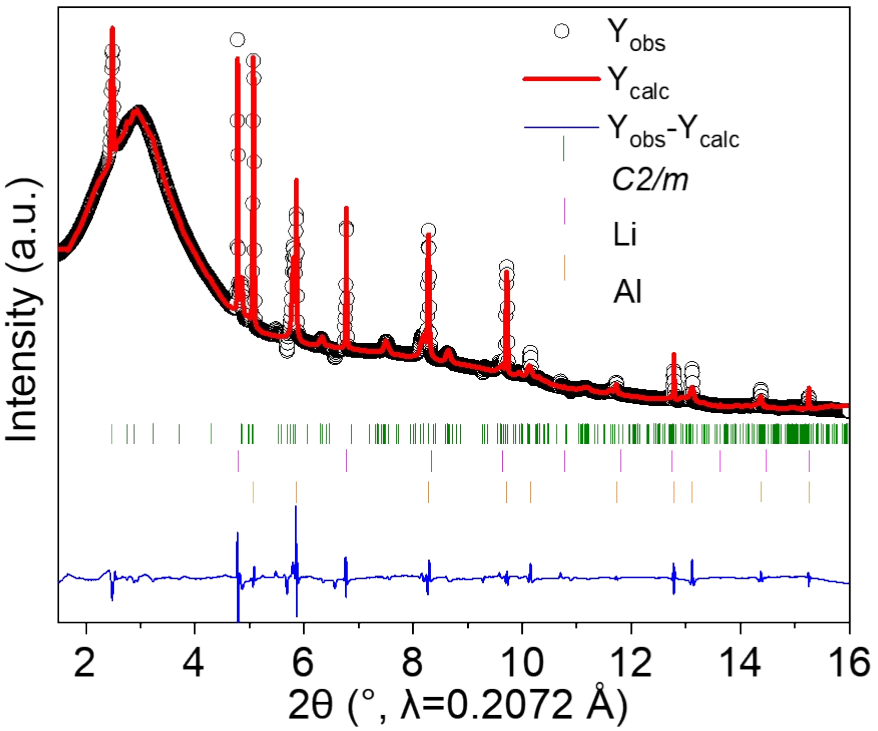

Figure S8. Rietveld refinement against sXRD pattern of LLNMO cathode discharged to 1.5 V.

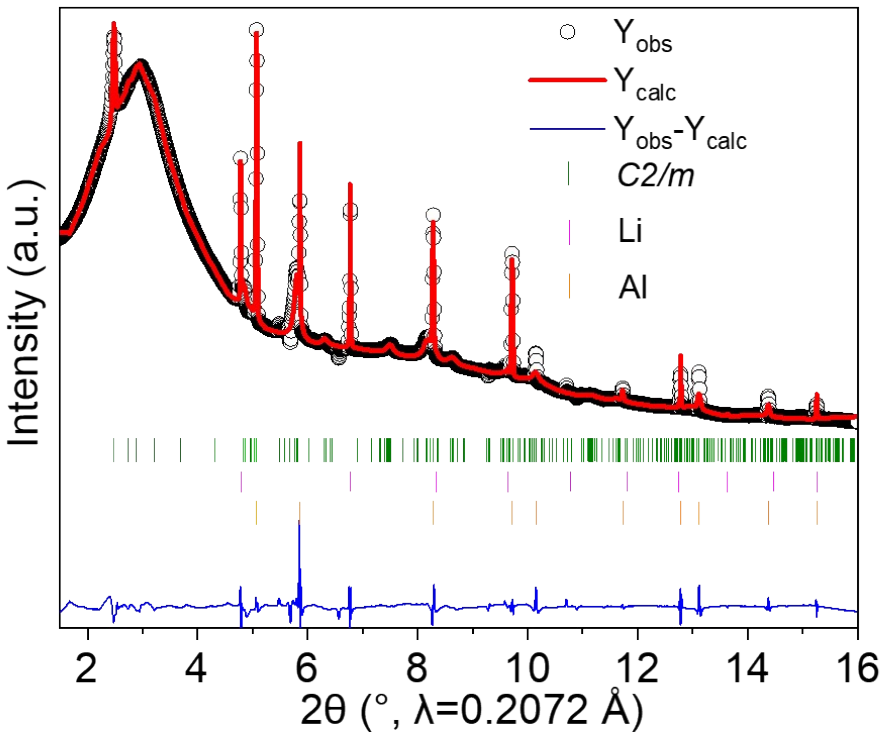

Figure S9. Rietveld refinement against sXRD pattern of LLNMO cathode discharged to 1.0 V.

Table S1. Element content of LLNMO sample.

Sample	Molar ratio		
	Li	Ni	Mn
LLNMO	1.18	0.21	0.61

Table S2. Crystallographic parameters of LLNMO.

Cell parameters

Space group: *C2/m*, a = 4.9611 (2) Å, b = 8.5948 (3) Å, c = 5.0318 (5) Å, V = 202.9234 (7) Å^3, beta = 108.952 (5)°

Atomic positions

Name	site	x	y	z	Fract
Li1	2c	0.000	0.000	0.500	1.000
Li2	4h	0.000	0.695	0.500	0.957
Ni2	4h	0.000	0.695	0.500	0.043
Ni1	2b	0.000	0.500	0.000	0.202
Li3	2b	0.000	0.500	0.000	0.410
Mn2	2b	0.000	0.500	0.000	0.396
Mn1	4g	0.000	0.1743	0.000	0.705
Ni3	4g	0.000	0.173	0.000	0.155
Li4	4g	0.000	0.173	0.000	0.149
O1	4i	0.216	0.000	0.223	1.000
O2	8j	0.250	0.332	0.228	1.000

Refinement parameters

R_{wp}= 1.12 %, R_p= 2.06 %, χ^2: 3.33