Revealing the Optimal Pre-lithiation Threshold of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ Cathode for Stable Anode-Free Lithium Metal Batteries

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Experimental Section

Material Preparation

The pre-lithiated NCM811 cathodes were prepared via a controlled electrochemical process. First, coin cells were assembled in an argon-filled glovebox using commercial NCM811 cathode sheets on a carbon-coated aluminum foil as the working electrode, lithium metal as the counter/reference electrode, and a standard liquid electrolyte. The pre-lithiation procedure was conducted as follows: the cells were initially cycled at 0.1 C for one full charge-discharge cycle to determine the specific discharge capacity (C_0). Subsequently, to achieve the desired pre-lithiation levels (Li1.25(NCM), Li1.5(NCM), Li1.75(NCM), and Li2.0(NCM)), the cells were subjected to a controlled over-discharge (lithiation) process. This was done by continuing the discharge at 0.1 C to a capacity equivalent to a specific percentage of the previously measured C_0. After the pre-lithiation was complete, the cells were disassembled carefully inside the glovebox. The retrieved cathode electrodes were thoroughly rinsed with DMC solvent to remove residual lithium salts and then dried under vacuum. Finally, these pre-lithiated cathodes were pair with bare copper foil anodes to assemble the AFLMBs for subsequent electrochemical testing.

Material Characterization

Scanning electron microscopy (SEM) imaging analyses were carried out on a ZEISS Sigma 300 field-emission microscope operating at 20 kV. X-ray diffraction (XRD) patterns were acquired over a 2θ range of 10°-80° with Cu Kα radiation using a PANalytical Empyrean diffractometer. X-ray photoelectron spectroscopy (XPS)

spectra were obtained using a Thermo Scientific K-Alpha spectrometer equipped with an Al Kα X-ray source (1486.6 eV).

Electrochemical Measurements

Coin-type cells (CR2032) were assembled for electrochemical testing. The working electrode was fabricated by homogenously dispersing active material, conductive carbon black (Super P, Alfa-Aesar), and polyvinylidene fluoride binder (PVDF, Sigma-Aldrich) in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 8:1:1. The resultant slurry was doctor-bladed onto pre-cleaned carbon-coated aluminum foil, vacuum-dried at 90°C for 12 h, and subsequently punched into 10 mm diameter discs with an active material loading of ~2.0 mg cm^{-2}. Lithium metal foil (for half-cell) and copper foil (for AFLMB) served as both counter and reference electrodes, with a Celgard polypropylene separator and electrolyte comprising 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v). All electrochemical characterizations were conducted at 25 ± 0.5 °C in a climate chamber using a LANDCT2001A battery testing system and Bio-Logic VMP3 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements employed a 10 mV AC amplitude across 10^{6}-10^{-2} Hz.

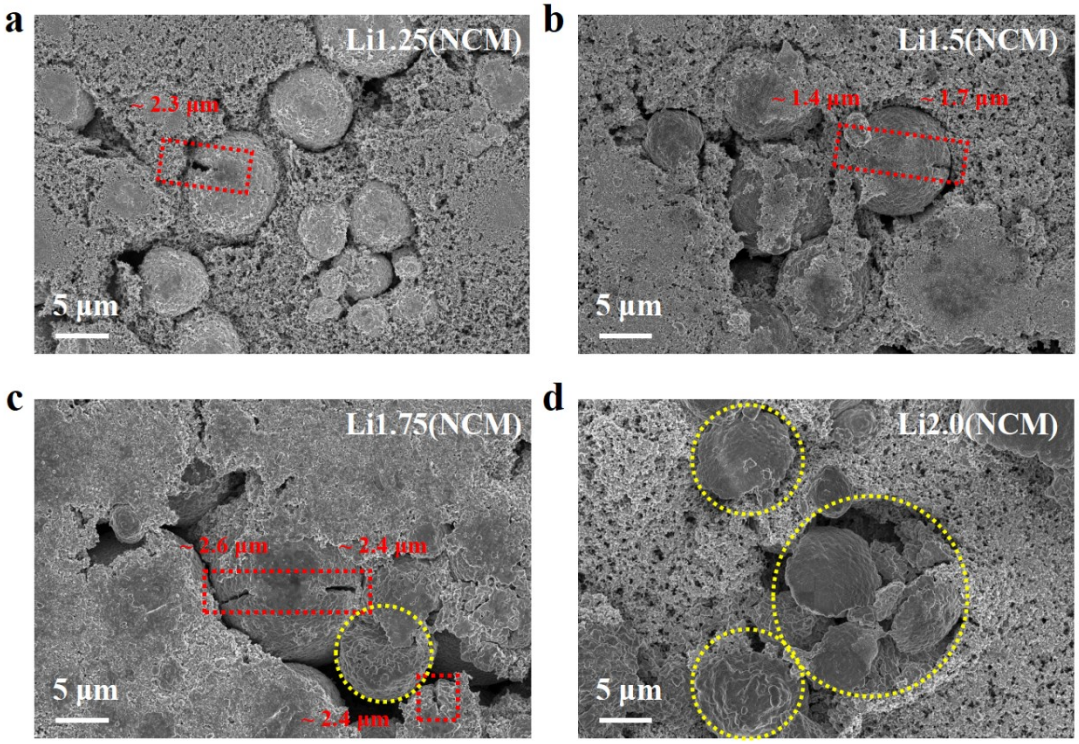
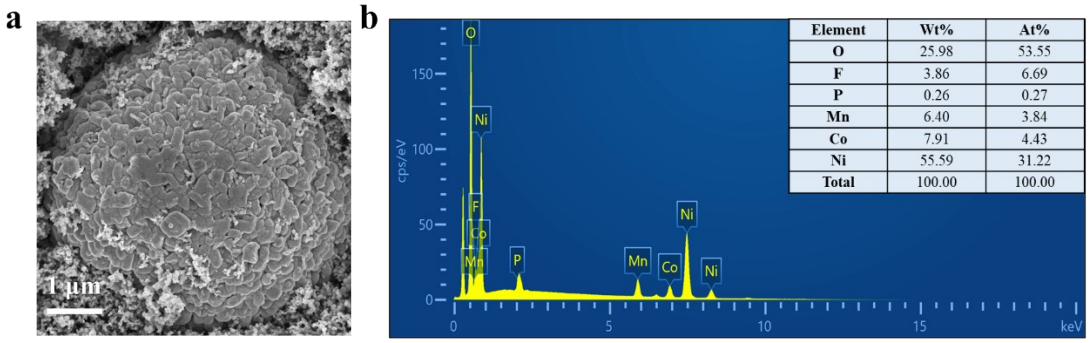
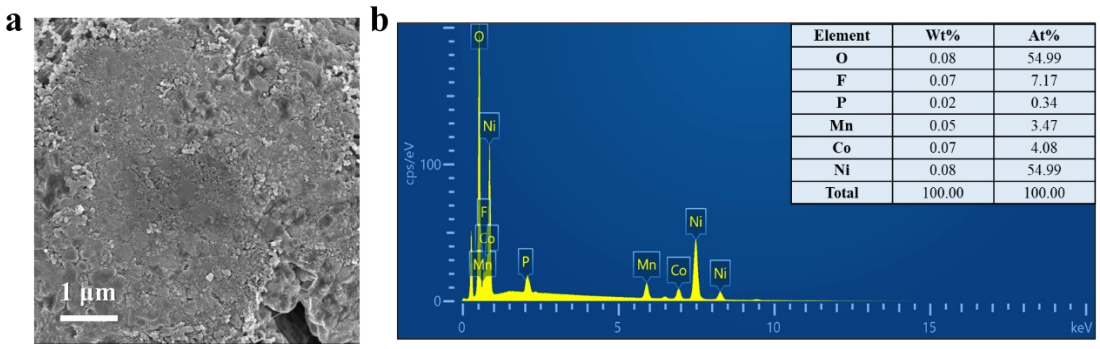


Fig. S1 SEM images of four pre-lithiated cathodes and crack length annotation.



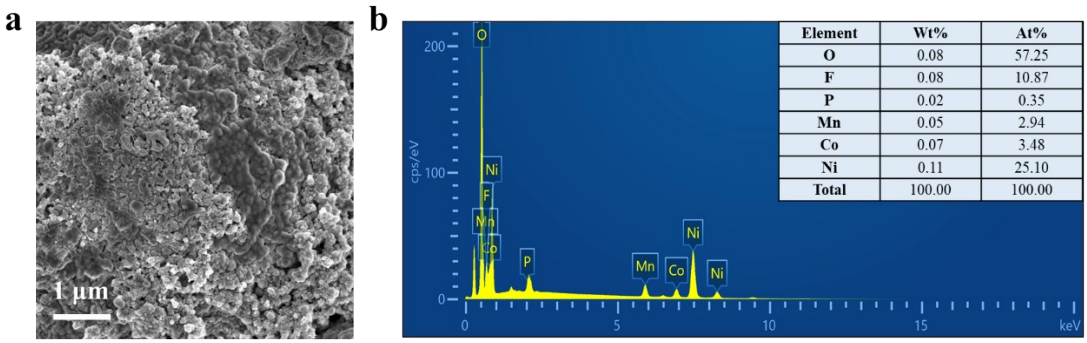
Element	Wt%	At%
O	25.98	53.55
F	3.86	6.69
P	0.26	0.27
Mn	6.40	3.84
Co	7.91	4.43
Ni	55.59	31.22
Total	100.00	100.00

Fig. S2 (a) SEM image and (b) EDS spectrum of Li1.0(NCM) electrode.



Element	Wt%	At%
O	0.08	54.99
F	0.07	7.17
P	0.02	0.34
Mn	0.05	3.47
Co	0.07	4.08
Ni	0.08	54.99
Total	100.00	100.00

Fig. S3 (a) SEM image and (b) EDS spectrum of Li1.25(NCM) electrode.



Element	Wt%	At%
O	0.08	57.25
F	0.08	10.87
P	0.02	0.35
Mn	0.05	2.94
Co	0.07	3.48
Ni	0.11	25.10
Total	100.00	100.00

Fig. S4 (a) SEM image and (b) EDS spectrum of Li1.5(NCM) electrode.

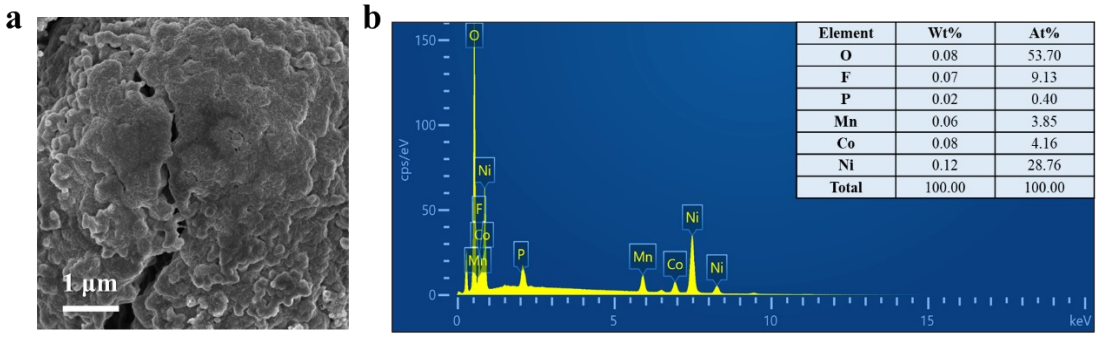
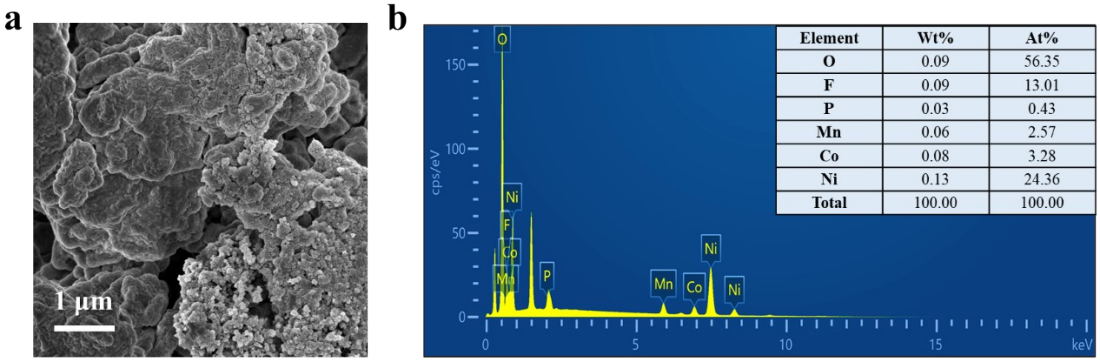


Fig. S5 (a) SEM image and (b) EDS spectrum of Li1.75(NCM) electrode.



Element	Wt%	At%
O	0.09	56.35
F	0.09	13.01
P	0.03	0.43
Mn	0.06	2.57
Co	0.08	3.28
Ni	0.13	24.36
Total	100.00	100.00

Fig. S6 (a) SEM image and (b) EDS spectrum of Li2.0(NCM) electrode.

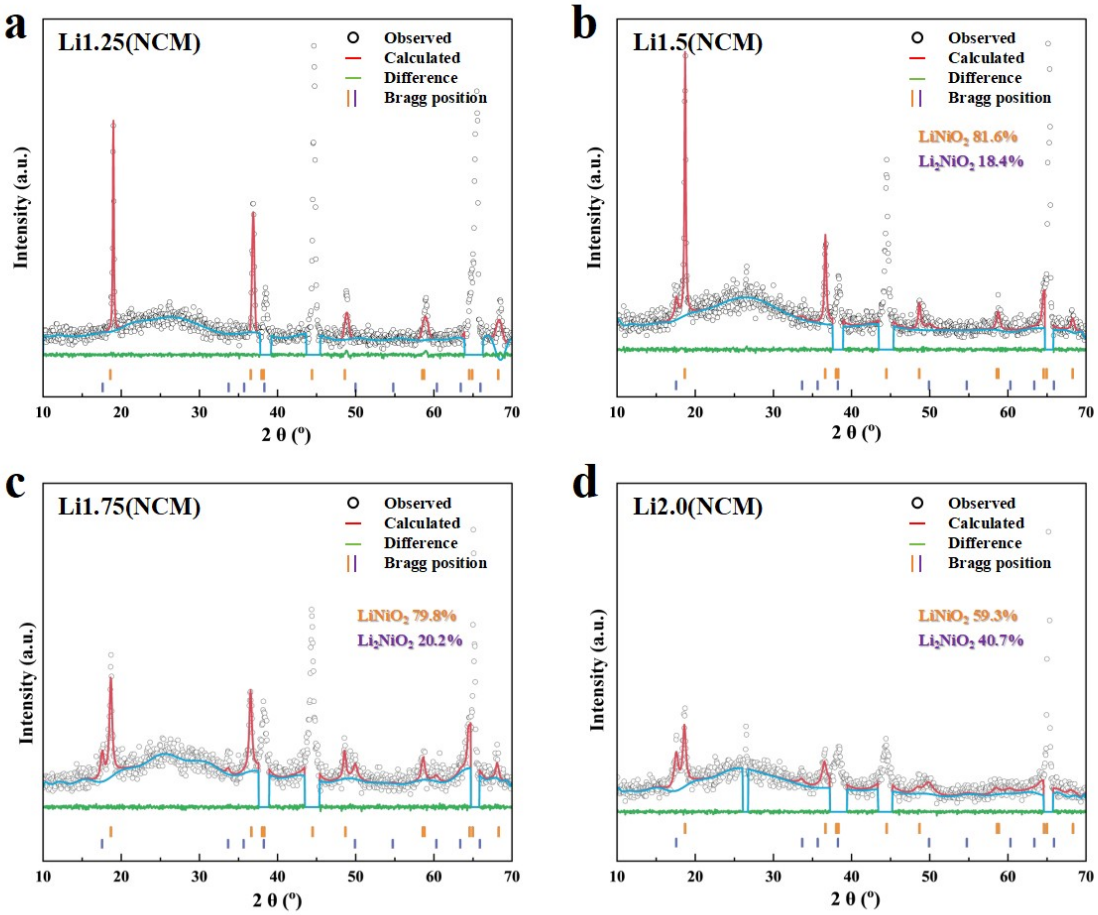


Fig. S7 Rietveld refinement of the XRD patterns for the four samples.

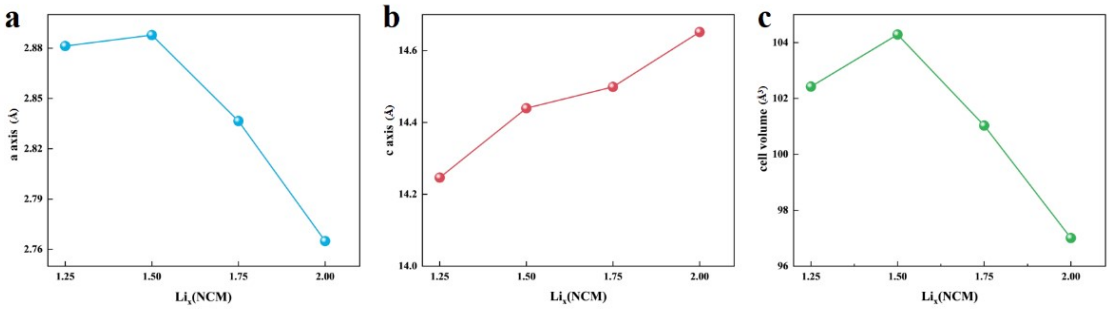


Fig. S8 Lattice parameters derived from Rietveld refinement.

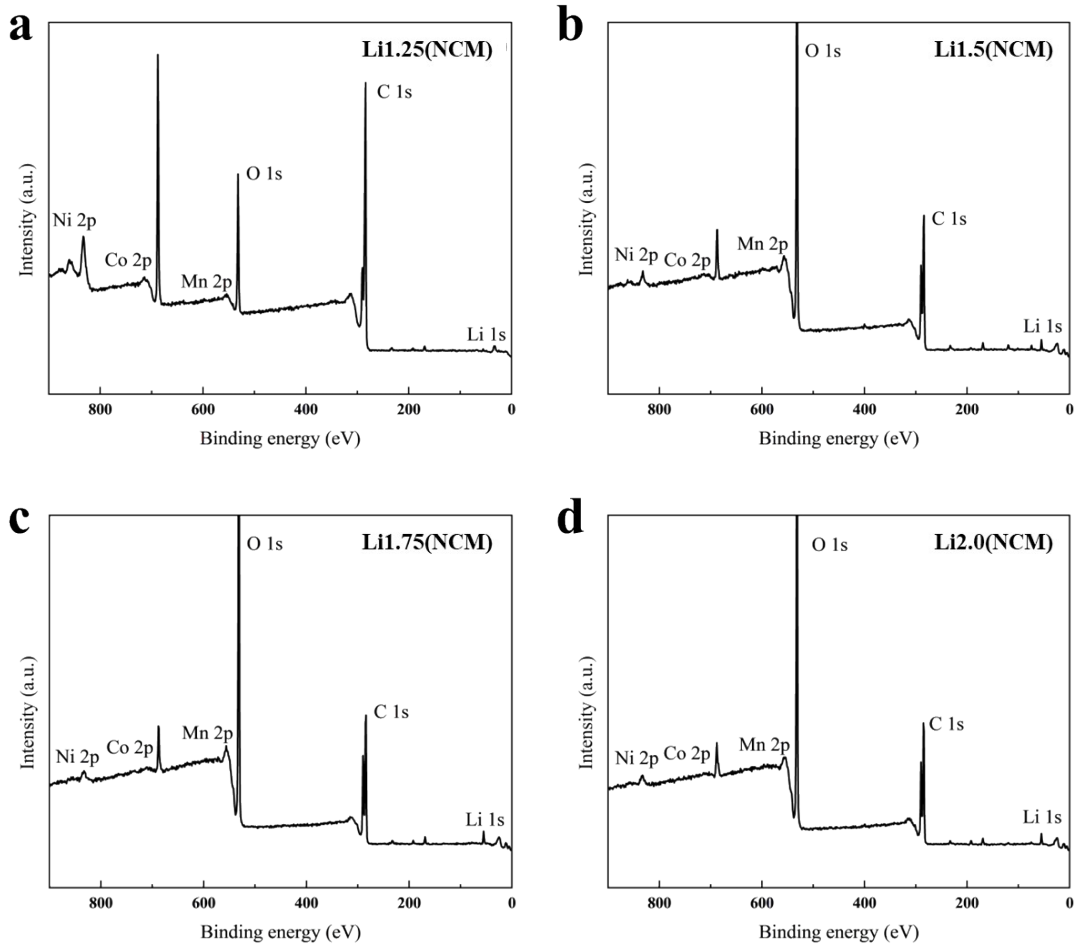


Fig. S9 XPS survey of (a) Li1.25(NCM), (b) Li1.5(NCM), (c) Li1.75(NCM) and (d) Li2.0(NCM) electrodes.

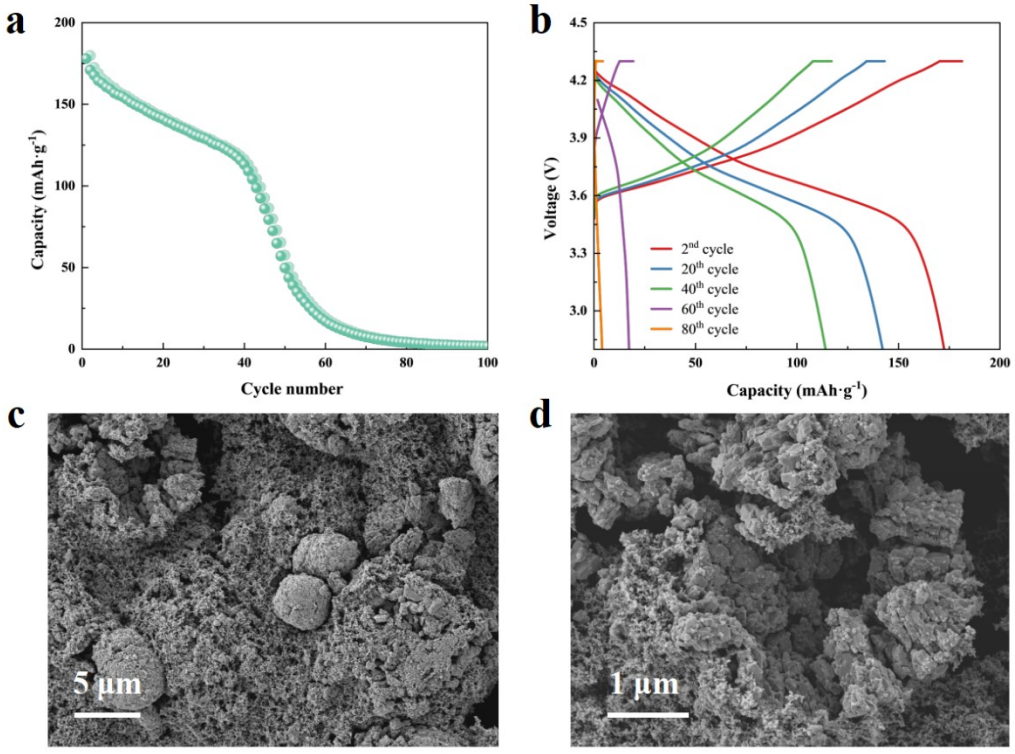


Fig. S10 (a) Cycling performance of Li1.5(NCM)||Cu cell. (b) Voltage-capacity profiles of various cycles. (c-b) SEM images of cycled Li1.5(NCM) electrode.

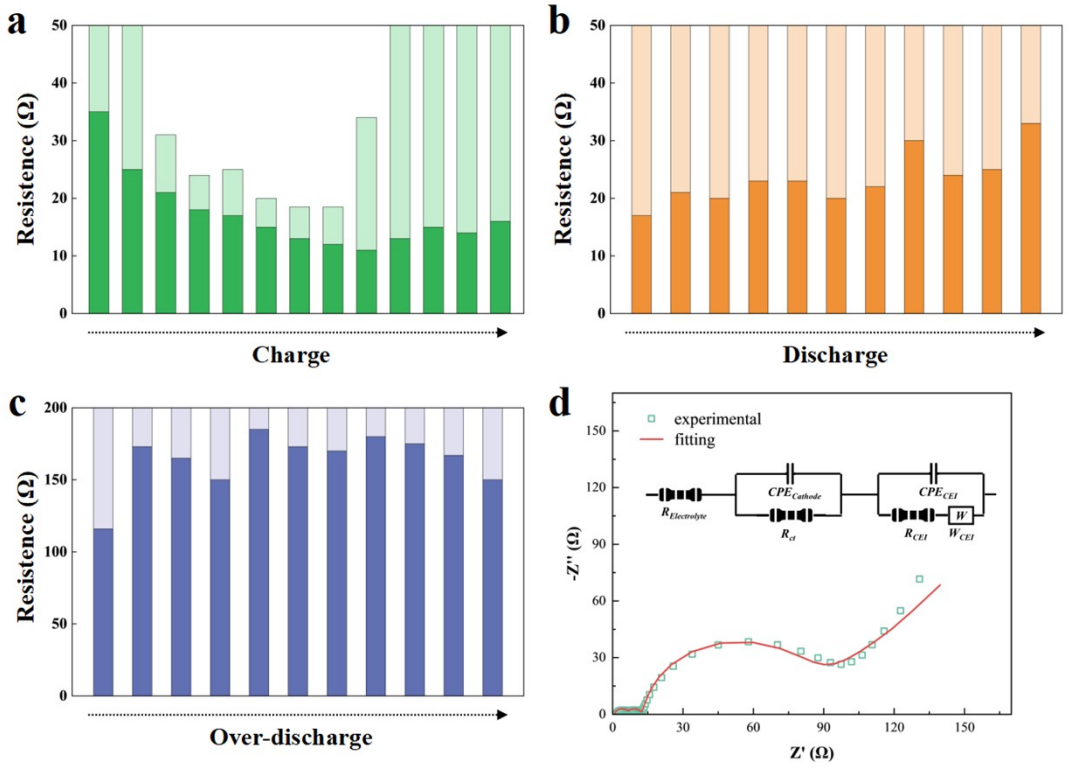


Fig. S11 Enlarged charge-transfer (R_{ct}) resistances obtained from fitting the in-situ EIS data during (a) charge, (b) discharge, and (c) over-discharge to Li2.0(NCM). (d) Equivalent circuit model and a representative Nyquist plot with fitting result.

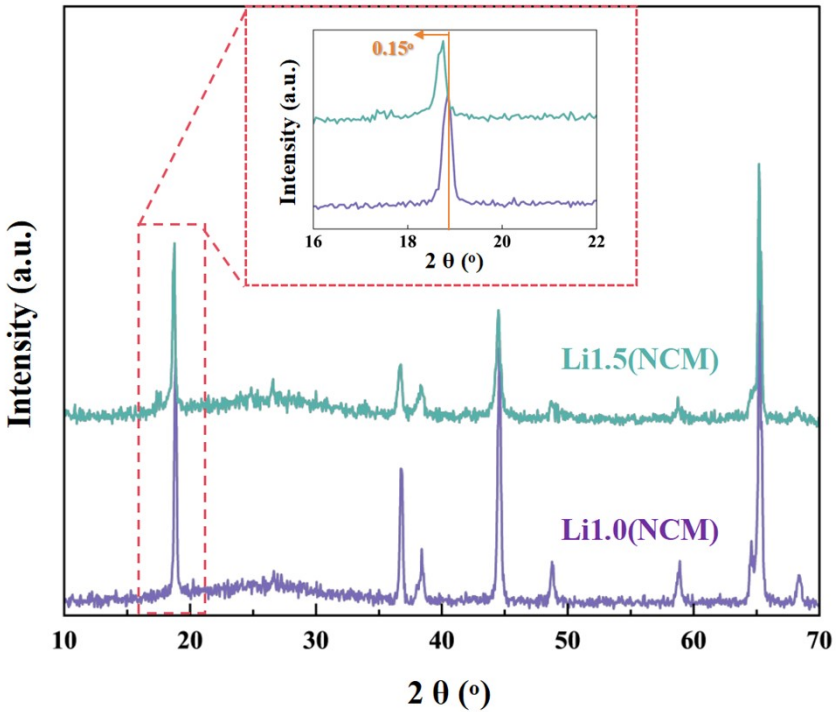


Fig. S12 Ex situ XRD pattern of Li1.0(NCM) and Li1.5(NCM) electrodes.

Table S1 Summary of the lattice parameters obtained from Rietveld refinement for the pre-lithiated cathodes

Sample	a axis (Å)	c axis (Å)	cell volume ($Å^3$)
Li1.25(NCM)	2.881294	14.24641	102.4263
Li1.5(NCM)	2.887825	14.43954	104.286
Li1.75(NCM)	2.83656	14.49897	101.0303
Li2.0(NCM)	2.764959	14.6517	97.00549

Table S2 Characteristics of the four pre-lithiated cathodes.

Sample	Li_2NiO_2 phase ratio (%)	Prelithiated voltage (V)	Li anode (1C 100 cycles)		Cu anode (1C 30 cycles)	
			Initial capacity ($mAh \cdot g^{-1}$)	Capacity retention (%)	Initial capacity ($mAh \cdot g^{-1}$)	Capacity retention (%)
Li1.25 (NCM)	/	1.71	142.8	74.2%	163.3	3.8%
Li1.5 (NCM)	18.4%	1.69	216.9	71.3%	187.9	33.2%
Li1.75 (NCM)	20.2%	1.03	117.2	49.5%	164.1	31.1%
Li2.0 (NCM)	40.7%	0.95	99.8	52.4%	160.8	19.2%