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Supplemental Information

Aluminium Doping to Single-Crystal Nickel-Rich Cathodes: Insights into Electrochemical Degradation and Enhancement

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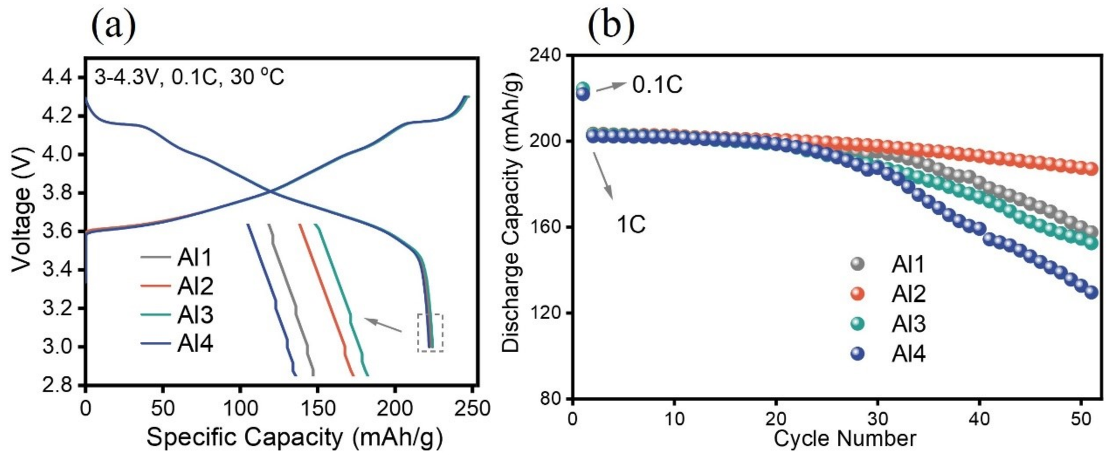

Fig. S1 Optimization of Al doping level, showing (a) the first cycle charge-discharge curves for different Al doping levels; (b) the capacity retention after 50 cycles. The different amounts of Al doping have a minor impact on the specific capacity during charging and discharging at 0.1C, but there is a noticeable difference in the material's cycle retention rate. Considering the enhancement of initial capacity and cycling performance, this paper selects Al2 as the material for subsequent experiments.

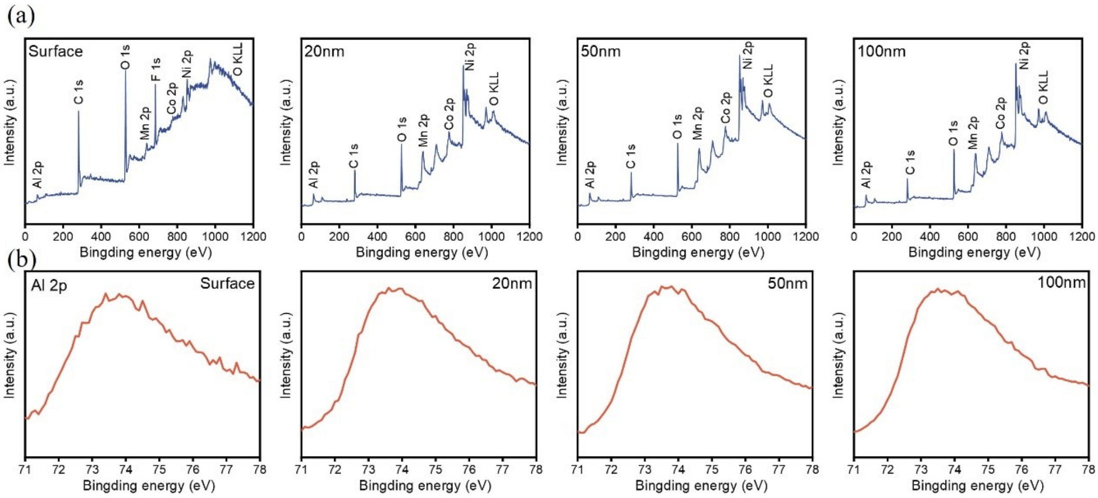

Fig. S2 The NCMA material at various etching depths features: (a) comprehensive XPS spectral data; (b) Al 2p XPS data. It is important to note that the electrode was utilized for XPS sample preparation. Consequently, the F 1s peak in the comprehensive XPS spectral data originates from polyvinylidene difluoride (PVDF), used as a binder, while the carbon is derived from acetylene black, employed as a conductive agent.

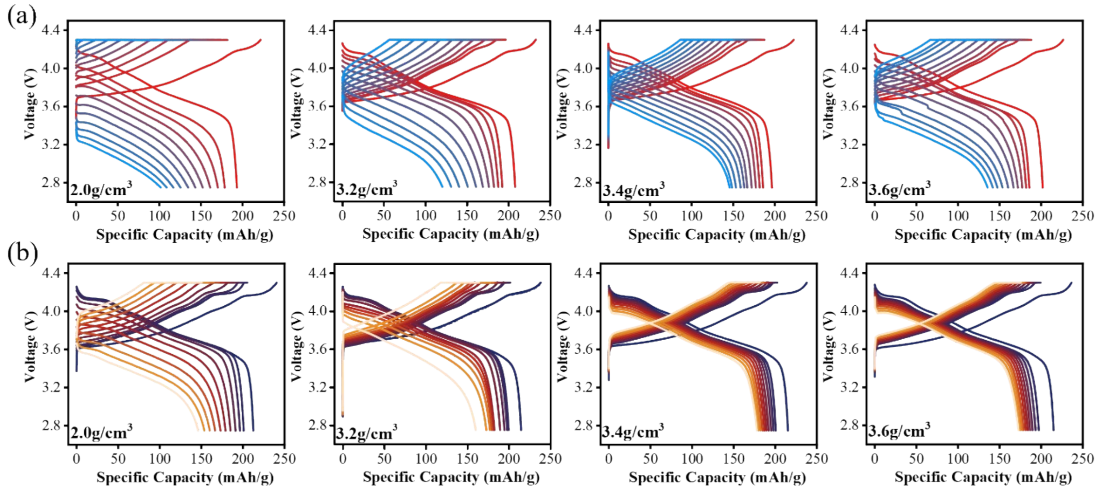

Fig. S3 Charge and discharge curves of NCM (a) and NCMA (b) Materials at different compaction densities from 2.0 g/cm³ to 3.6 g/cm³.

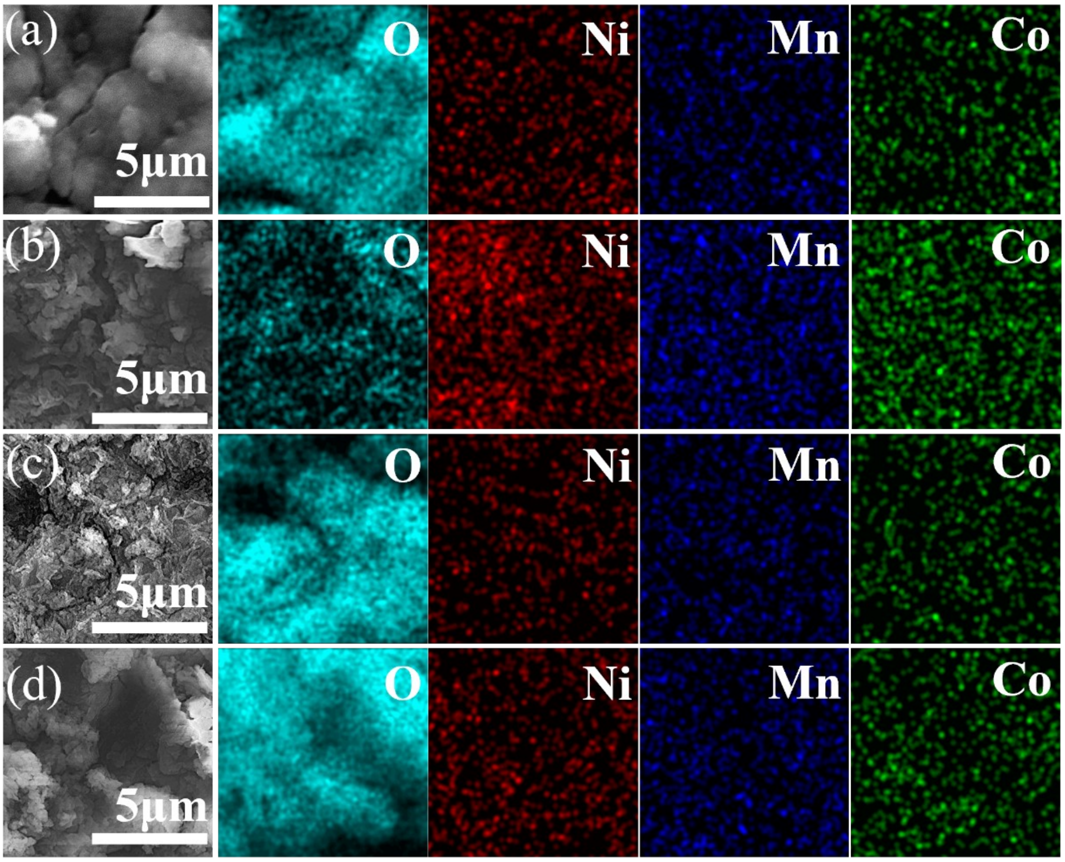

Fig. S4 Post-Cycling Anode Microstructure and Composition: SEM and EDS Insights at Varied Voltages: (a-b) with NCM cathode at 4.3V and 4.5V; (c-d) With NCMA cathode at 4.3V and 4.5V.

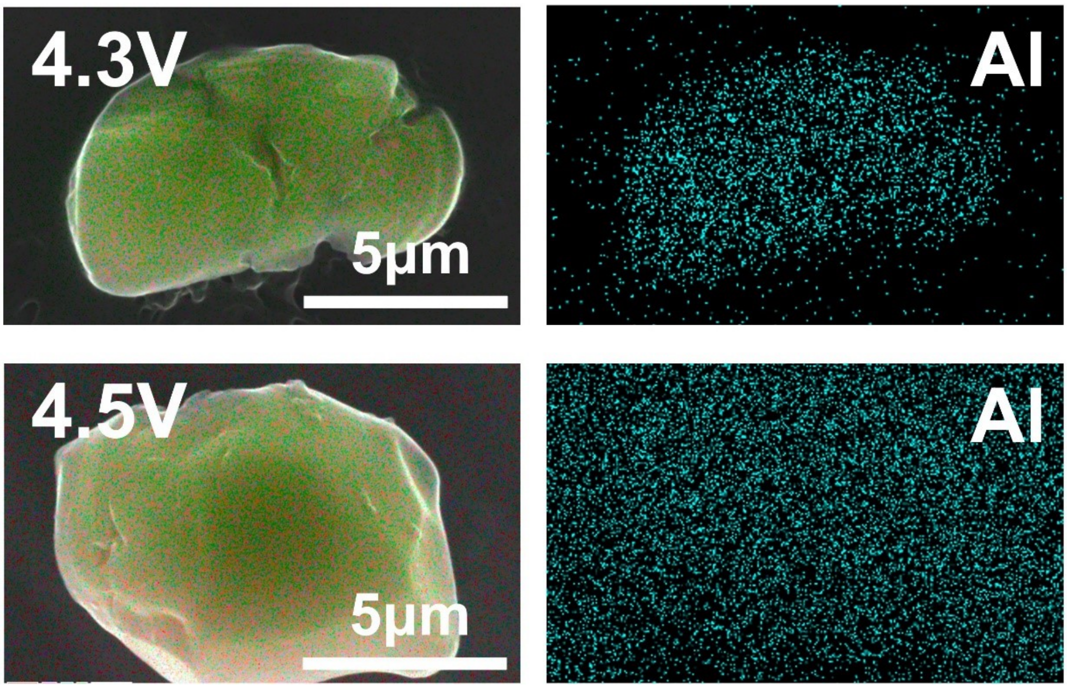

Fig. S5 SEM images and EDS spectra of the NCMA material after 100 cycles at cut-off voltages of 4.3V and 4.5V, respectively.

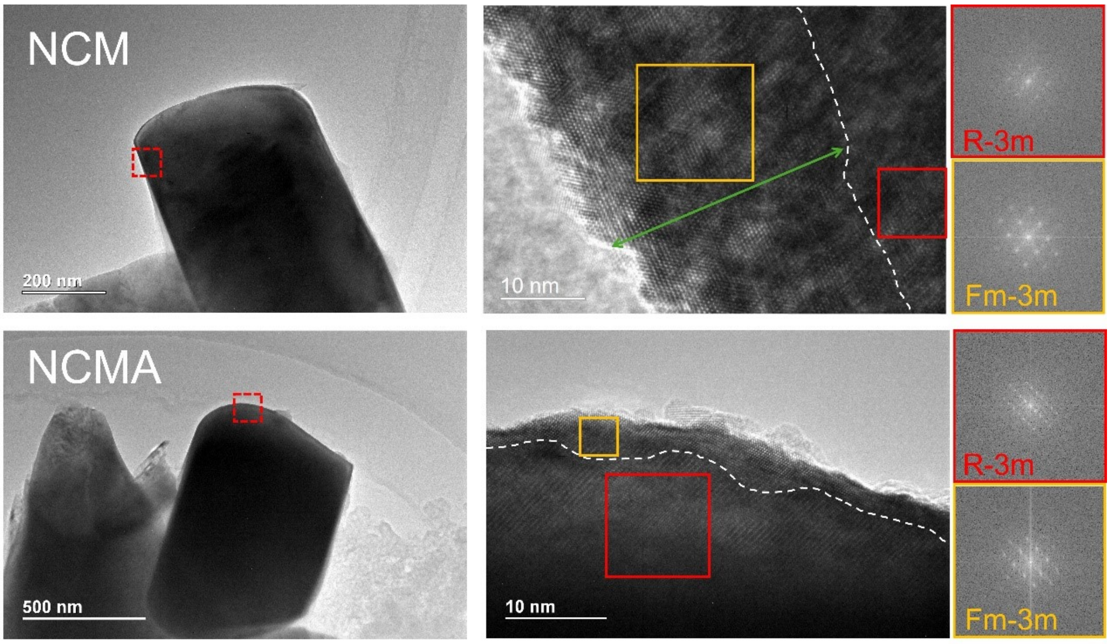

Fig. S6 TEM images for two other particles of NCM and NCMA, are provided to illustrate the phase transition states of the materials after 100 cycles.

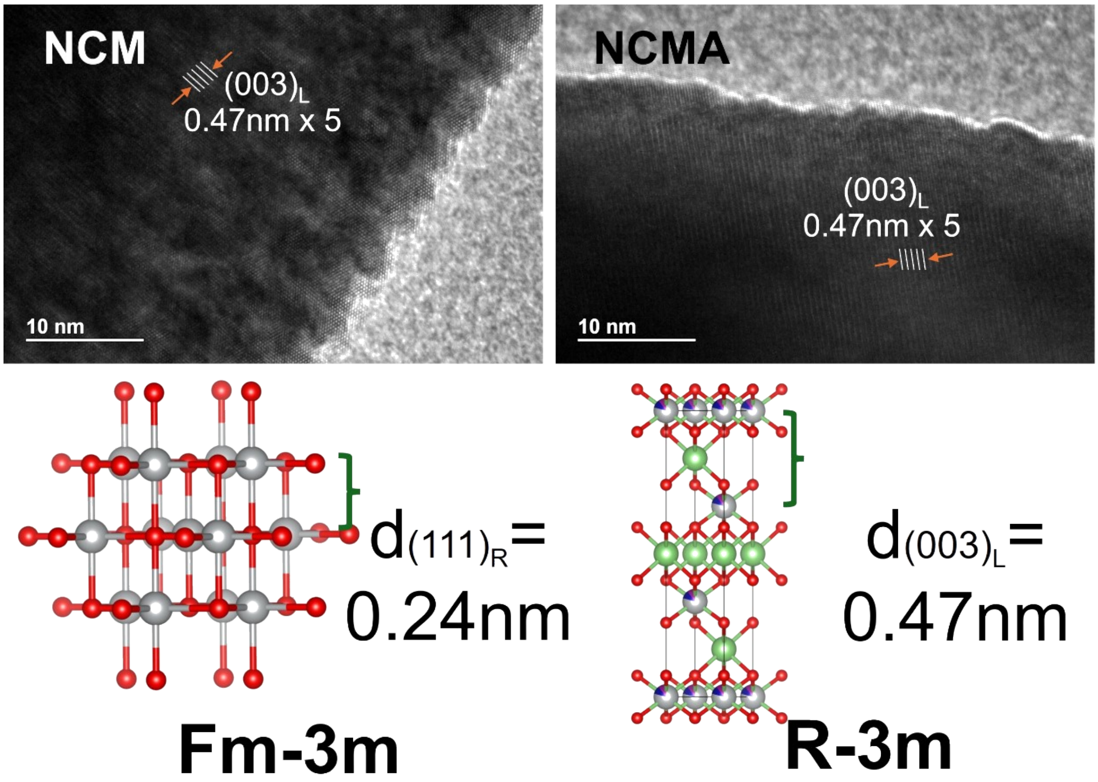

Fig. S7 Evidence of layered phase in NCM and NCMA after 100 cycles, as well as schematic diagrams illustrating the lattice spacing of rock-salt and layered phases.

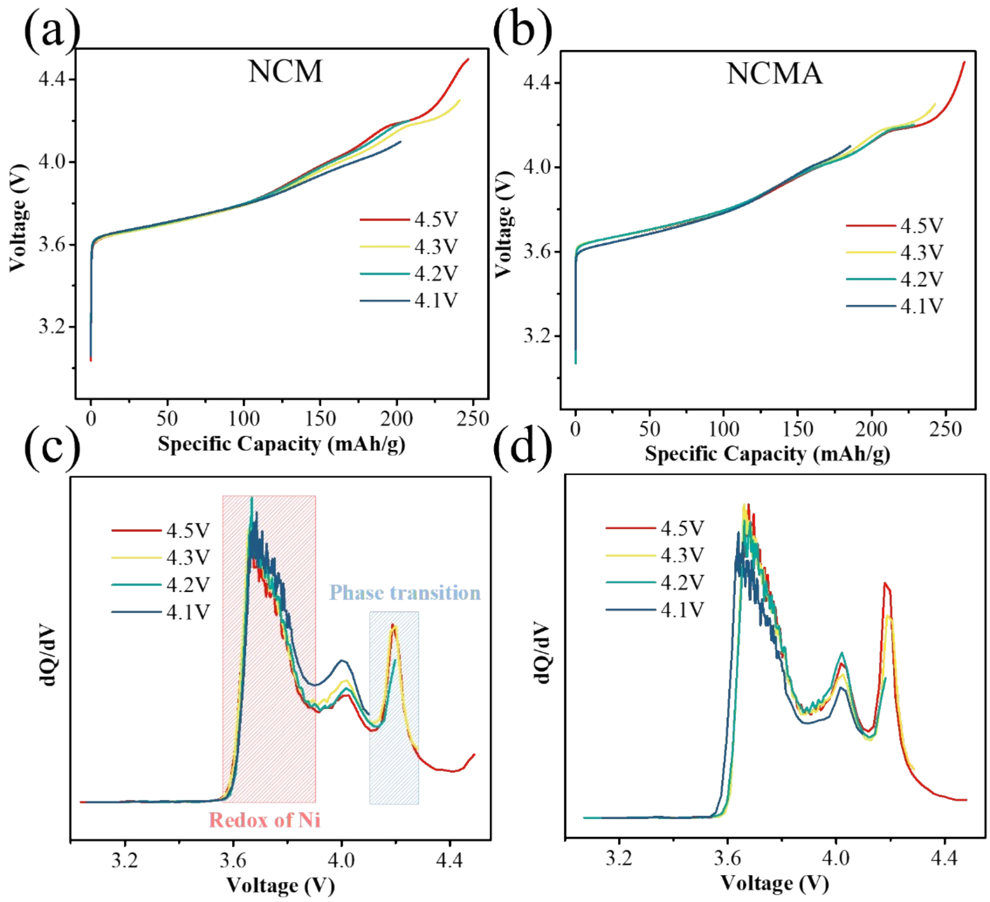

Fig. S8 Corresponding to the State-of-Charge Dependent XAS date, Initial Charge Profiles and Differential Capacity Analysis for Ni-rich Cathodes: (a-b) Charging behavior of NCM and NCMA; (c-d) dQ/dV curves for NCM and NCMA.

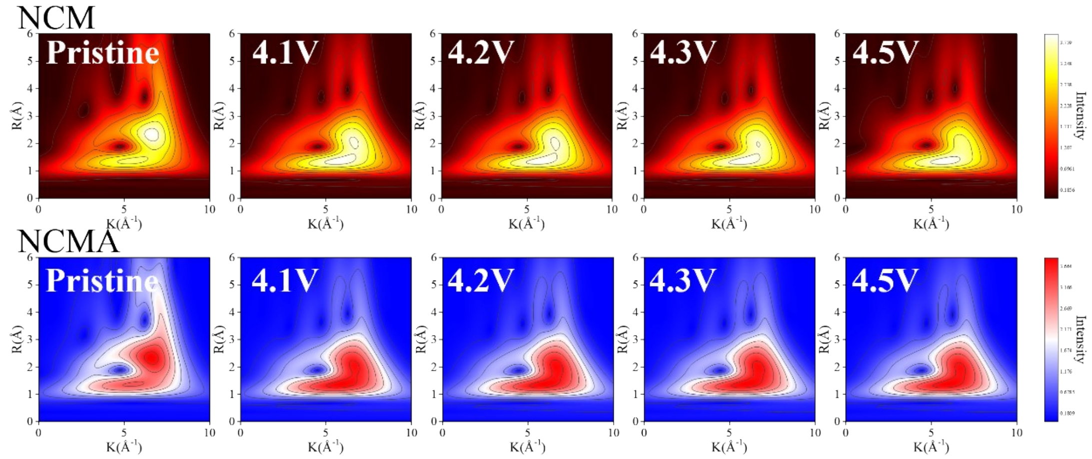

Fig. S9 Wavelet Analysis of Ni K-edge EXAFS for High-Coordination Environments: The contour plots visualize the strength of the Morlet wavelet transform applied to k2-weighted extended X-ray absorption fine structure (EXAFS) signals, revealing the coordination structure around nickel atoms.

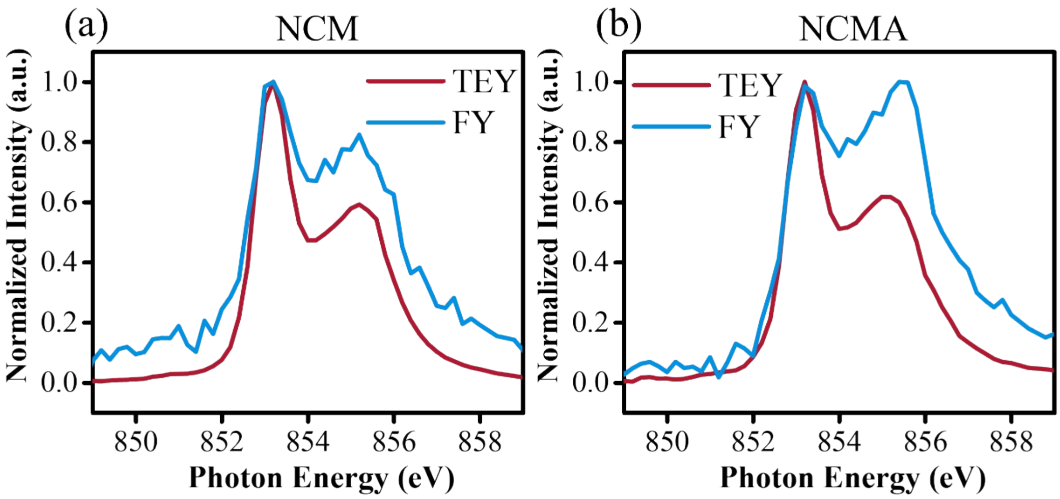

Fig. S10 Differential Analysis of Nickel L-edge X-ray Absorption Spectroscopy in Total Electron Yield and Fluorescence Yield Modes for Cathode Materials (a) NCM and (b) NCMA.

Table. S1 Literature Review on Quaternary NCMA or Al Elements Doping Nickel-rich Cathode Materials

Ref.	Capacity (mAh/g)	Capacity retention	Morphology	Main characterization	Highlights
1	228 (0.1C)	90.6% (2.7-4.3V, 0.5C, 100 cycles)	PC	SEM TEM DSC	NCM-NCMA
2	223 (0.1C)	94.2% (3-4.3v, 0.5C/1C, 100 cycles)	SC	SEM TEM DSC	Synthesis
3	204 (0.1C)	88% (3-4.3V, n/a, 50 cycles)	PC	SEM TEM XPS	Modification (doping&coating)
4	210 (0.1C)	76.4% (3-4.4V, 1C, 200 cycles)	PC	SEM XRD XPS	Al concentration
5	221 (0.1C)	74% (2.7-4.3V, 1C, 100 cycles)	PC	SEM TEM XRD XPS	Modification (coating)
6	200 (0.1C)	74.6% (2.8-4.3V, 1C, 100 cycles)	PC	SEM TEM XRD XPS	Modification (coating)
7	200 (1C)	73.1% (2.7-4.3V, 1C, 100 cycles)	SC	SEM TEM XRD in-situ XRD XPS TOF-SIMS	Modification (coating)
8	214 (0.1C)	77% (2.7-4.3V, 1C, 100 cycles)	PC	SEM TEM XRD XPS	Modification (gradient)
9	161.4 (0.5C)	85% (2.8-4.3V, 0.5C, 80 cycles)	PC	SEM XRD	Synthesis
10	213.9 (0.1C)	45% (2.8-4.3V, 0.5C, 100 cycles)	PC	SEM XRD	Modification (doping)
11	225 (0.1C)	94% (3-4.3v, 0.5C, 100 cycles)	PC	SEM XRD	Al concentration
12	220 (0.1C)	68% (2.7-4.3v, 1C, 100 cycles)	PC	SEM XRD XPS	Role of Co and Mn
13	212 (n/a)	74.92% (3-4.3v, 1C, 300 cycles)	PC	SEM XRD XPS TEM AFM	NCM-NCMA
14	200 (0.1C)	80% (3-4.4V, 1C, 90 cycles)	SC	SEM XRD TEM	Al concentration
15	205 (0.1C)	100% (2.8-4.4V, 0.1C, 100 cycles)	PC	SEM XRD in-situ XRD	NCM-NCMA
16	n/a	n/a	n/a	DFT	Role of Co, Mn and Al
17	180 (0.1C)	78.92% (2.7-4.3v, 1C, 200 cycles)	PC	SEM TEM XPS XRD	Synthesis methods
18	163 (1C)	83.42 (2.7-4.3v, 1C, 100 cycles)	PC	SEM TEM XPS XRD	Modification (doping&coating)
19	180 (0.1C)	92% (3-4.3V, 1C, 70 cycles)	PC	SEM XRD	Modification (co-doping)
This work	**224 (0.1C)**	**85.9% (2.75-4.3V, 1C, 100 cycles)**	**SC**	**SEM TEM XRD soft/hard-XAS EXAFS XPS**	**NCM-NCMA**

Table. S2 Refined structural parameters of NCM based on R-3m model

a(Å)	*b*(Å)	*c*(Å)	alpha(°)	beta(°)	gamma(°)	volume(Å^3)
2.868162	2.868162	14.16363	90	90	120	100.905
element	occupancy	x	y	z	uiso	
Li1	0.9765	0	0	0.5	0.025	
Ni1	0.0235	0	0	0.5	0.025	
Li2	0.0235	0	0	0	0.025	
Ni2	0.8565	0	0	0	0.025	
Mn1	0.0600	0	0	0	0.025	
Co1	0.0600	0	0	0	0.025	
O1	1.0000	0	0	0.266	0.025	

Table S3 Refined structural parameters of NCMA based on R-3m model

a(Å)	*b*(Å)	*c*(Å)	alpha(°)	beta(°)	gamma(°)	volume(Å^3)
2.872724	2.872724	14.180172	90	90	120	101.344
element	occupancy	x	y	z	uiso	
Li1	0.9888	0	0	0.5	0.025	
Ni1	0.0112	0	0	0.5	0.025	
Li2	0.0112	0	0	0	0.025	
Ni2	0.8621	0	0	0	0.025	
Al1	0.0200	0	0	0	0.025	
Mn1	0.0534	0	0	0	0.025	
Co1	0.0533	0	0	0	0.025	
O1	1.0000	0	0	0.257	0.025	

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