Supporting Information

Bulk Ca-doping induced surface modification enabling high performance O3-type layered cathode for sodium ion battery

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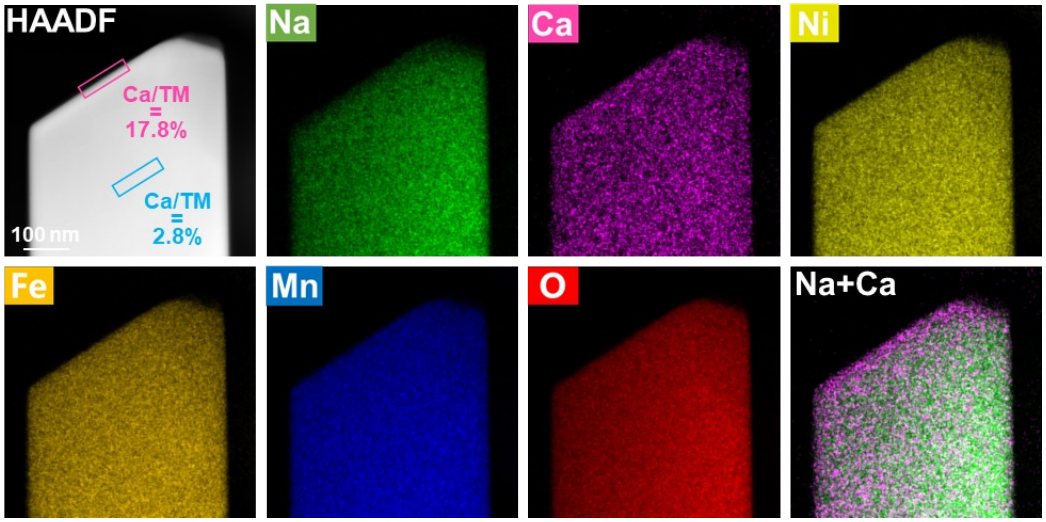

Figure S1. STEM-HAADF image of 5Ca-NFM and EDS-mapping of the corresponding Na, Ca, Ni, Fe, Mn, and O elements, showing Ca enrichment on the surface.

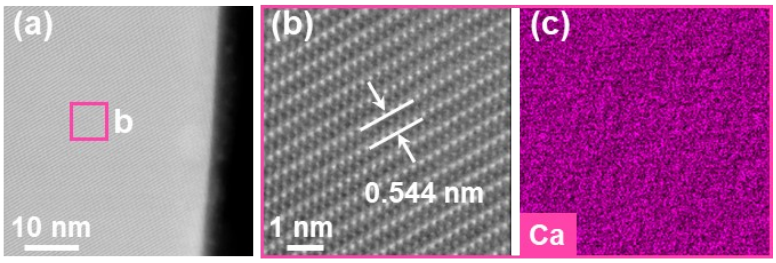

Figure S2. (a) Low-magnification STEM-HAADF image of the 3Ca-NFM. (b) Atomic resolution STEM-HAADF image and (c) EDS-mapping of Ca element of bulk phase.

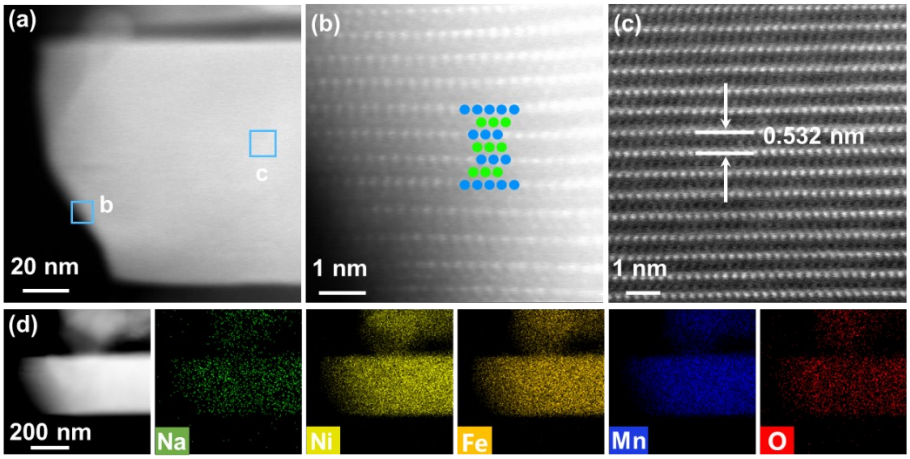

Figure S3. (a) STEM-HAADF image of undoped NFM sample. High resolution images from the grain (b) non-(003) surface and (c) bulk. (d) STEM-HAADF image of NFM and EDS-mapping of the corresponding Na, Ni, Fe, Mn, and O elements.

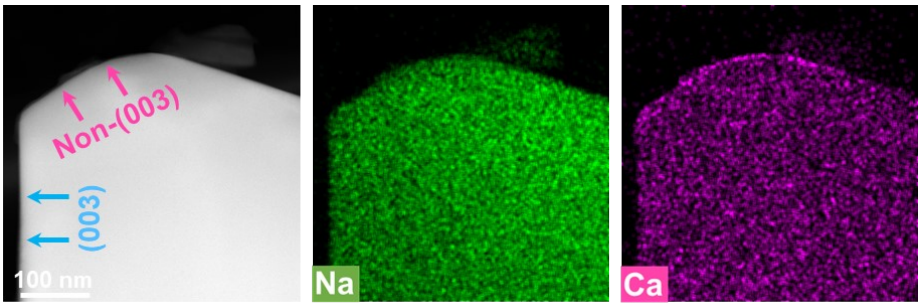

Figure S4. STEM-HAADF image of 3Ca-NFM and EDS-mapping of the corresponding Na and Ca elements, showing Ca enrichment on the surface.

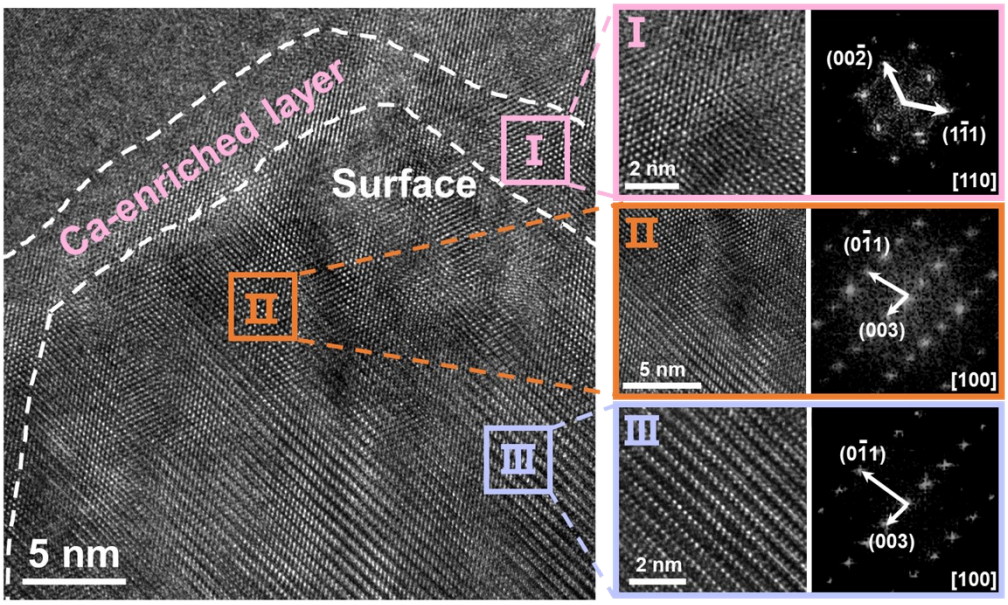

Figure S5. HRTEM images of the surface and bulk phase of the 3Ca-NFM and the corresponding FFT images.

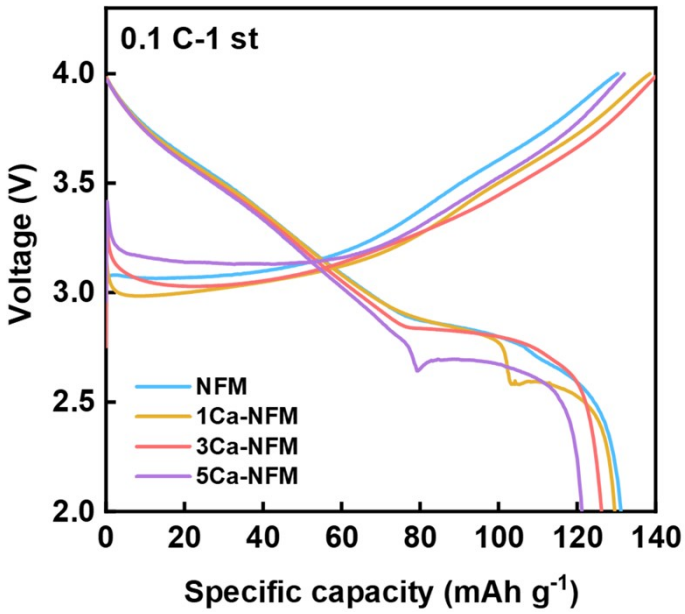

Figure S6. First cycle charge/discharge curves of all samples at 0.1 C rate.

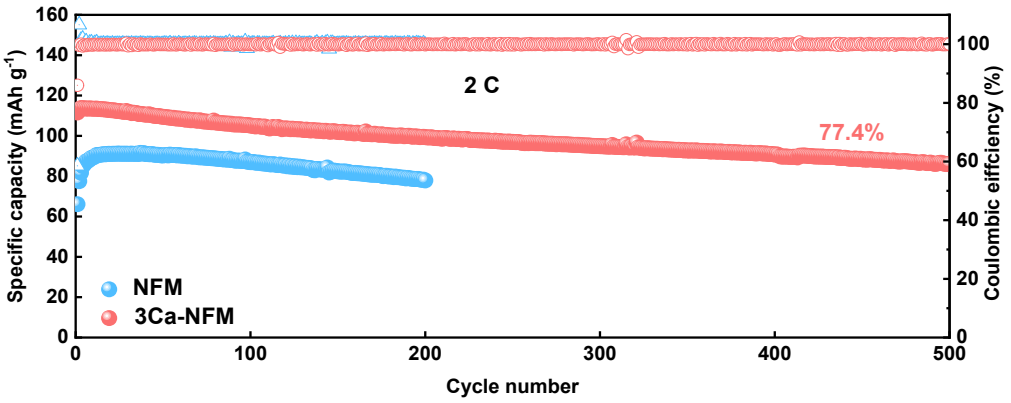

Figure S7. Capacity retentions of NFM and 3Ca-NFM cycling at 2 C (2.0-4.0 V).

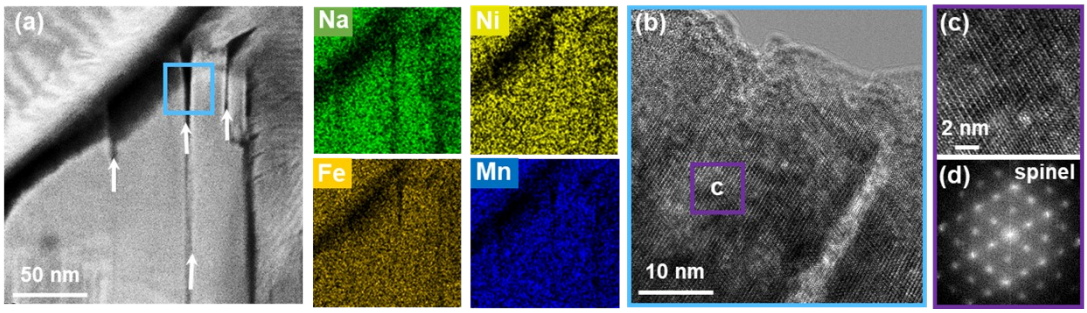

Figure S8. (a) STEM-HAADF image of NFM after 200 cycles and EDS-mapping of the corresponding Na, Ni, Fe, and Mn elements. (b) HRTEM images of the surface, (c) purple boxed region from (b). (d) FFT of the (c) region.

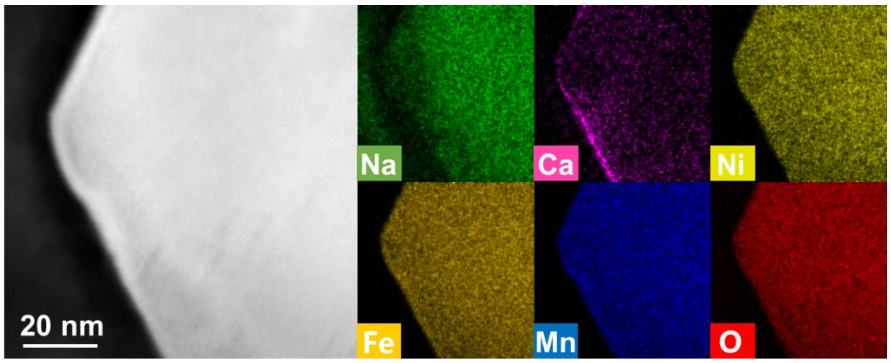

Figure S9. STEM-HAADF image and corresponding EDS-mapping of 3Ca-NFM after 200 cycles, showing Ca enrichment on the non-(003) surface.

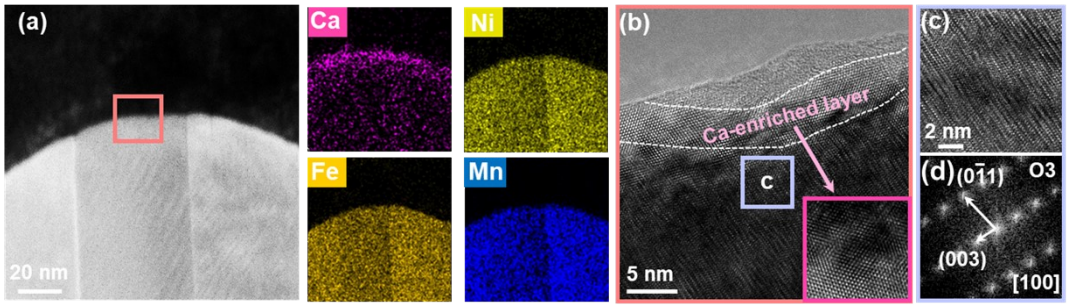

Figure S10. (a) STEM-HAADF image of 3Ca-NFM after 200 cycles and EDS-mapping of the corresponding Ca, Ni, Fe, and Mn elements. (b) HRTEM images of the surface with Ca-enriched layer of rock salt phase structure, (c) blue boxed region from (b). (d) FFT of the (c) region.

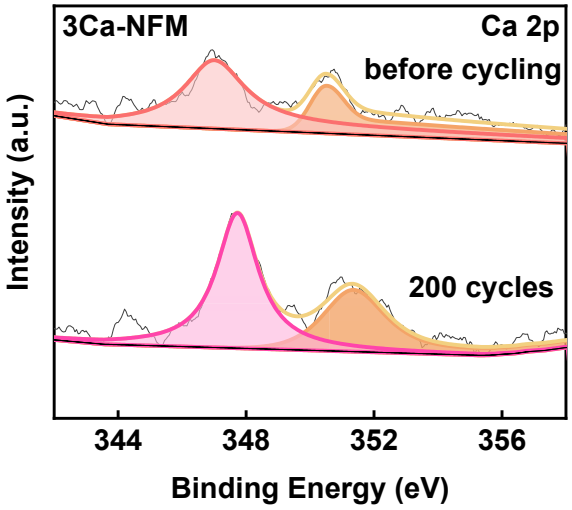

Figure S11. XPS spectra of Ca 2p for 3Ca-NFM before and after 200 cycles.

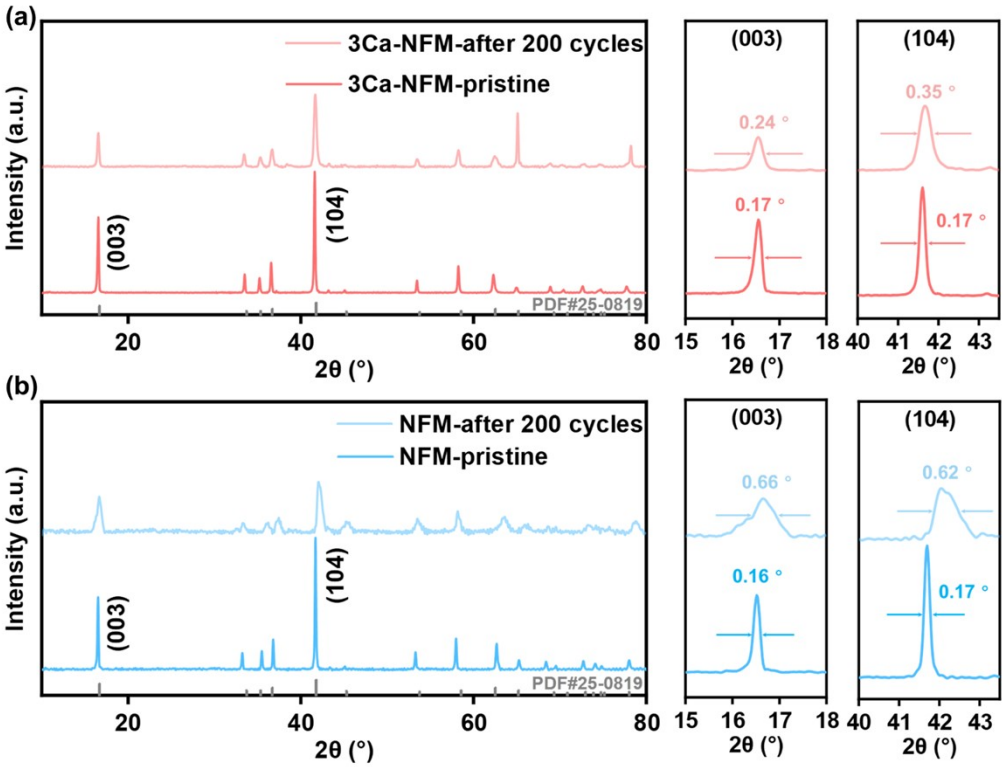

Figure S12. XRD pattern of pristine and after 200 cycles at 1 C of (a) 3Ca-NFM and (b) NFM cathodes, and the corresponding FWHM of the (003) and (104) peaks.

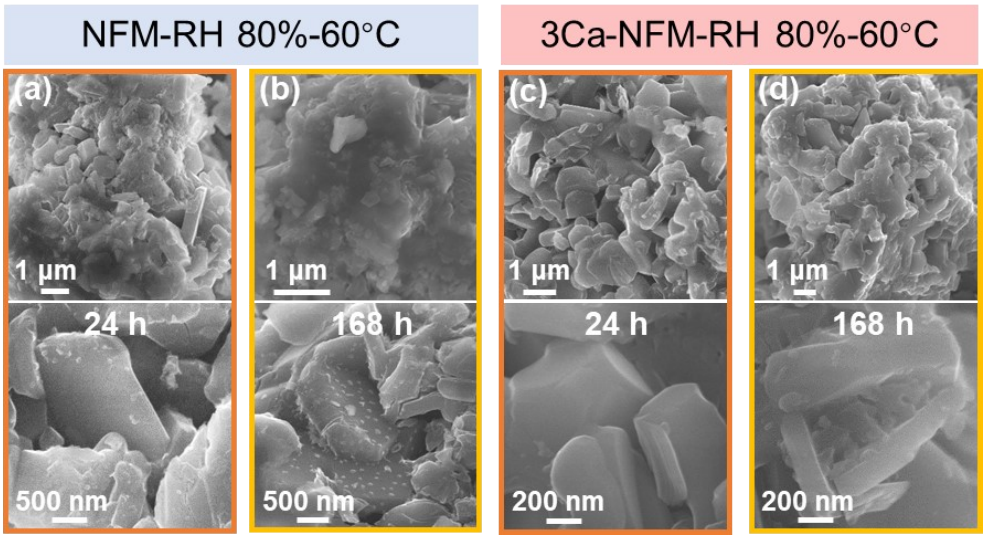

Figure S13. SEM images of NFM storage for (a) 24 h and (b) 168 h, and 3Ca-NFM storage for (c) 24 h and (d) 168 h at 60°C and 80% humidity.

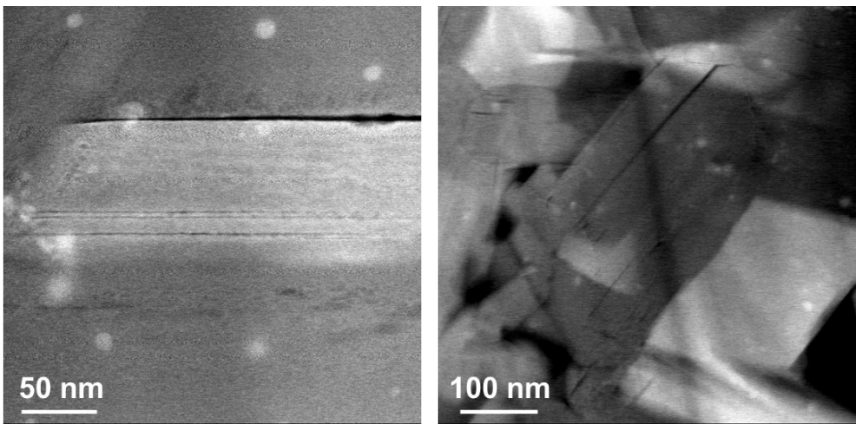

Figure S14. STEM-HAADDF images of NFM after 24 h storage at 60 °C and 80% humidity.

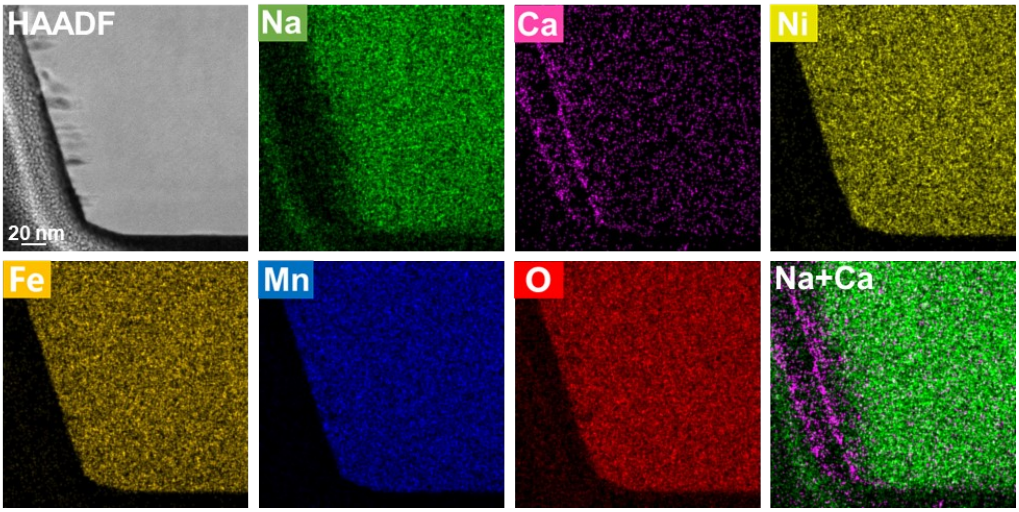

Figure S15. STEM-HAADDF images of 3Ca-NFM after 24 h storage at 60°C and 80% humidity and EDS-mapping of the corresponding Na, Ca, Ni, Fe, Mn, and O elements, showing Ca enrichment on the surface.

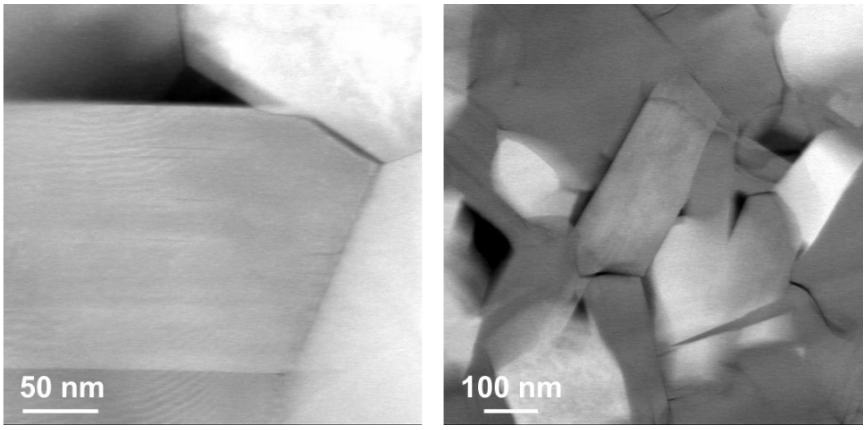

Figure S16. STEM-HAADDF images of 3Ca-NFM after 24 h storage at 60 °C and 80% humidity.

Table S1. ICP-AES results for NFM and 3Ca-NFM.

Sample	ICP (at%)			
	Ni	Fe	Mn	Ca
NFM	33.8	32.8	33.4	0
3Ca-NFM	33.3	32.2	34.5	2.98

Table S2. Summary of electrochemical performance of 3Ca-NFM and the published works with the similar O3-type cathodes.

Cycle voltage	Initial capacity	Cycle number	Capacity retention	Reference
2.1-3.9 V	122.1 mAh g^{-1} (0.1 C) 113 mAh g^{-1} (0.5 C)	200	83.4% (0.5 C)	1
2.0-4.0 V	137 mAh g^{-1} (0.1 C)	50	96.2% (1 C)	2
2.0-4.0 V	~115 mAh g^{-1} (0.1 C) ~108 mAh g^{-1} (1 C)	280	82.5% (1 C)	3
2.0-4.0 V	135.6 mAh g^{-1} (1 C) 124.6 mAh g^{-1} (2 C)	100	84.1% (2 C)	4
2.0-4.0 V	138.6 mAh g^{-1} (0.1 C) 120.1 mAh g^{-1} (1 C)	200	66.9% (1 C)	5
2.0-4.0 V	138 mAh g^{-1} (0.2 C)	50	85.8% (0.2 C)	6
1.5-4.0 V	~120 mAh g^{-1} (0.05 C)	100	86% (1 C)	7
2.0-4.0 V	126.9 mAh g^{-1} (0.1 C) 116.1 mAh g^{-1} (1 C)	200	91.8% (1 C)	8
2.0-4.0 V	126.0 mAh g^{-1} (0.1 C) 115.2 mAh g^{-1} (1 C)	200	90.5% (1 C)	This work

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