Supporting Information

Delineating the Capacity Fading Mechanisms of Na(Ni$_{0.3}$Fe$_{0.4}$Mn$_{0.3}$)O$_2$ at Higher Operating Voltages in Sodium-ion Cells

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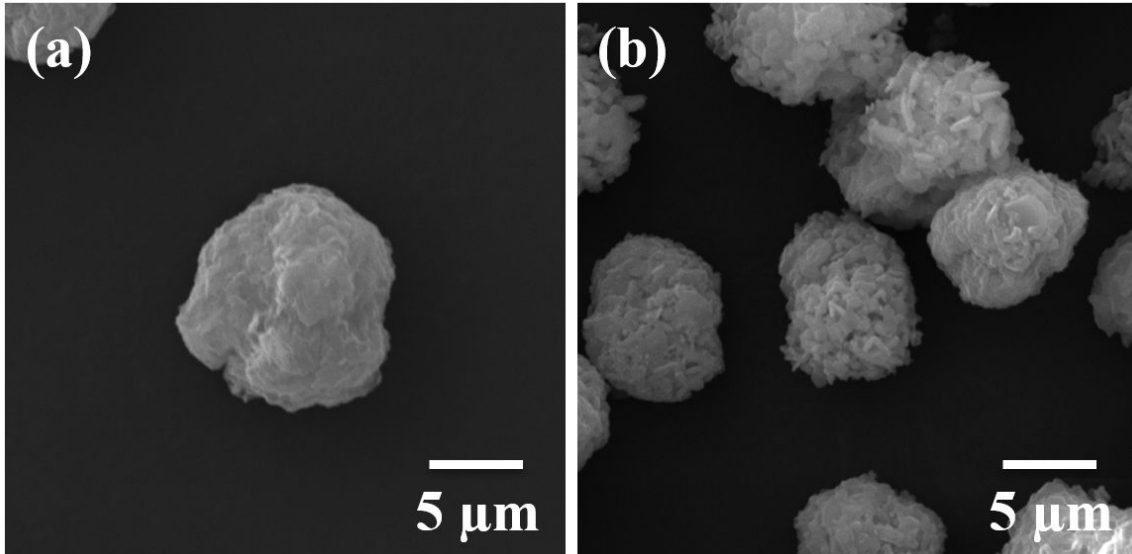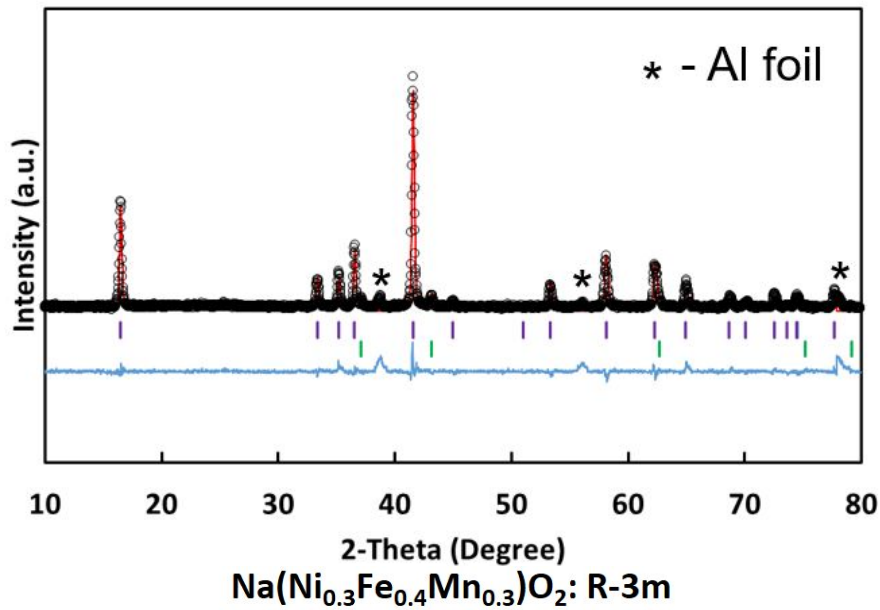
Figure S1. SEM images of (a) hydroxide M(OH) precursor and (b) pristine, calcined Na(Ni$_{0.3}$Fe$_{0.4}$Mn$_{0.3}$)O$_2$.

Na(Ni$_{0.3}$Fe$_{0.4}$Mn$_{0.3}$)O$_2$: R-3m

Atom	Site	x	y	z	Occ.
Na	-3m	0	0	0	1
Ni	-3m	0	0	1/2	0.3
Mn	-3m	0	0	1/2	0.3
Fe	-3m	0	0	1/2	0.4
O	3m	0	0	0.23478	1

a = 2.977232 Å; c = 16.094767 Å; V = 123.549 Å^3; R$_p$ = 15.665 %; R$_{wp}$ = 16.498 %

NiO Phase fraction: 7.32 %

Figure S2. Rietveld refinement and the associated crystallographic data of pristine O3 Na(Ni$_{0.3}$Fe$_{0.4}$Mn$_{0.3}$)O$_2$.
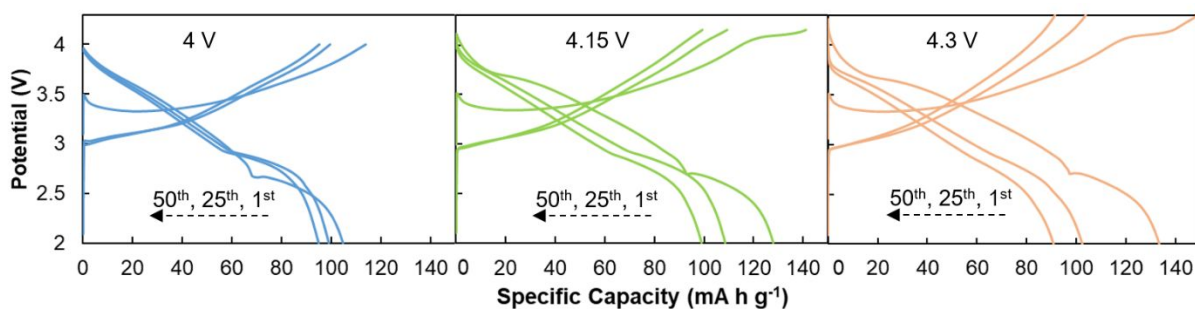
Figure S3. The 1st, 25th, and 50th charge-discharge profiles of NFM343 half cells charged up to varying voltages at a current rate of C/5.
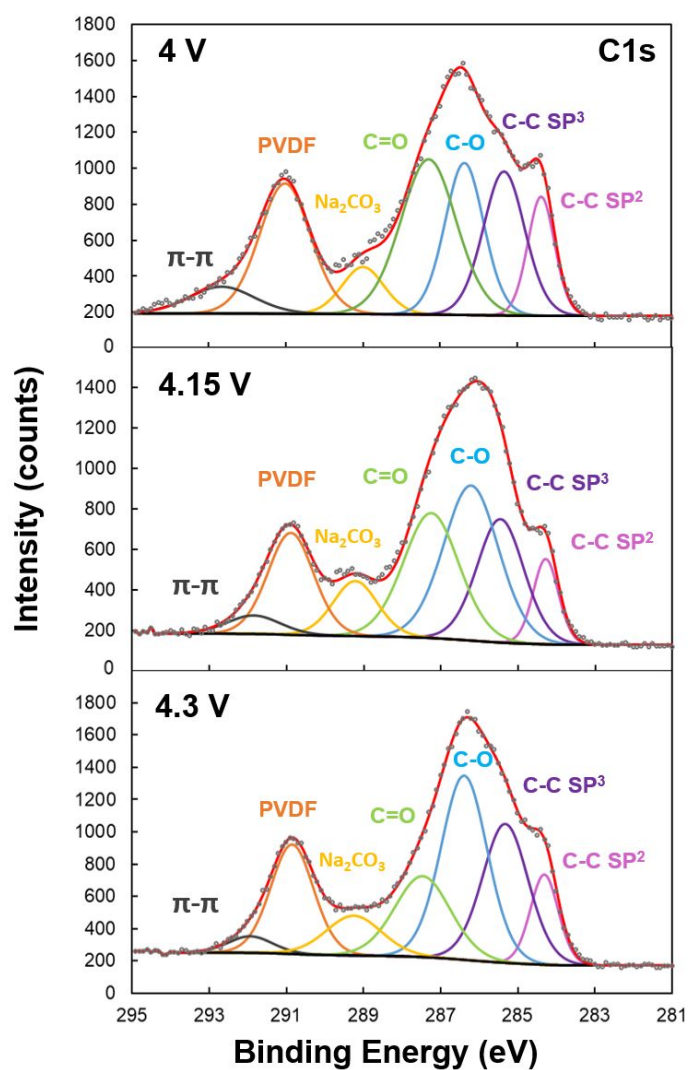

Figure S4. XPS data of the carbon (C1s) region performed on cathode material after 5 cycles.
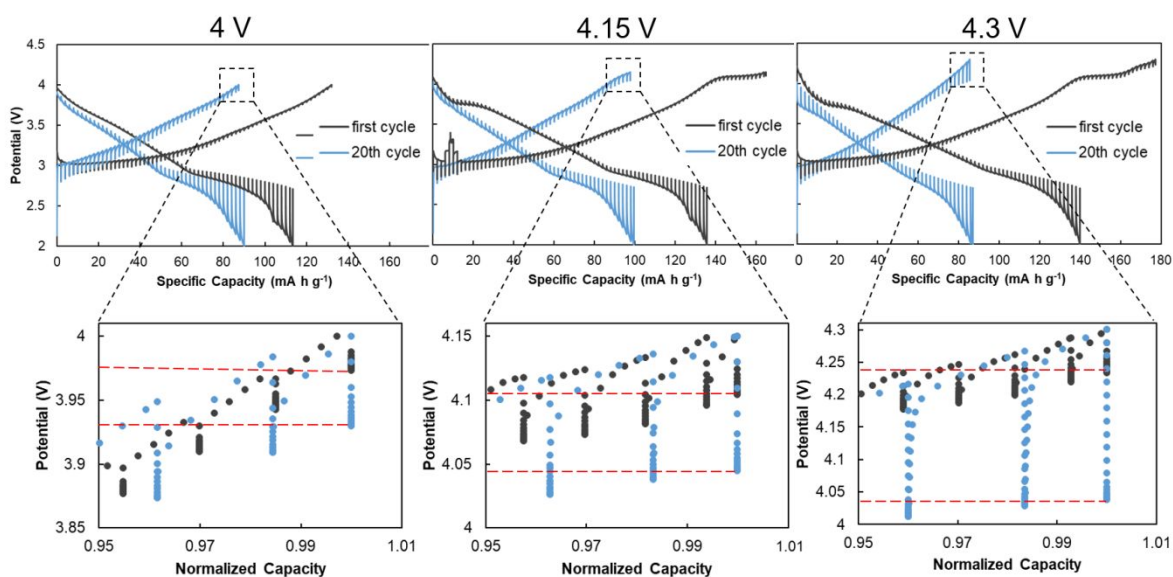
Figure S5. GITT on NFM charged to varying voltages with a 5 minute current step at C/5 rate, followed by a 10 minute rest step. Between the first and 20th GITT cycles, cells were cycled without intermittent resting at 1C rate. Bottom row shows the normalized capacity for direct comparison of impedance growth between the 1st and 20th cycle.
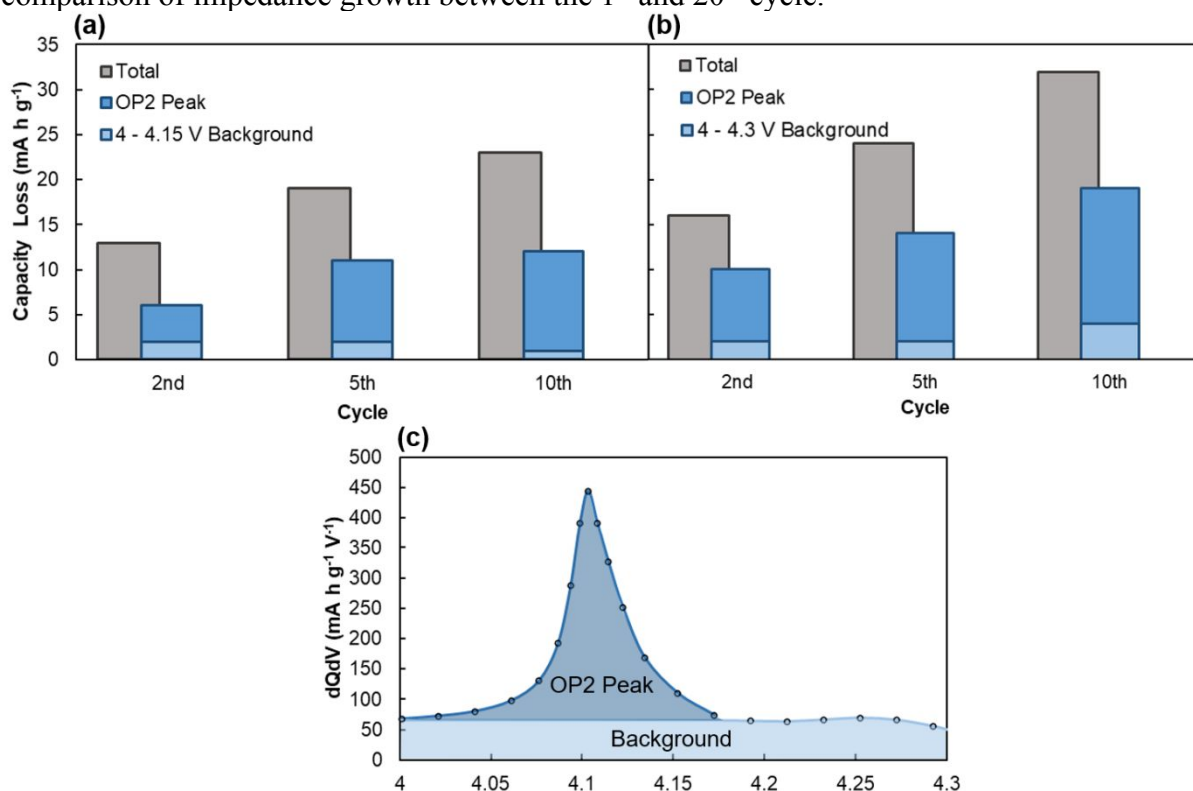

Figure S6. (a) and (b) Charge capacity lost between a given cycle and the first cycle when charged up to 4.15 and 4.3 V, respectively. Total capacity lost includes the entire voltage range, while the background and OP2 peak are constrained to the voltage region of > 4 V. (c) The background versus OP2 peak area on the first cycle of a 4.3 V cell.
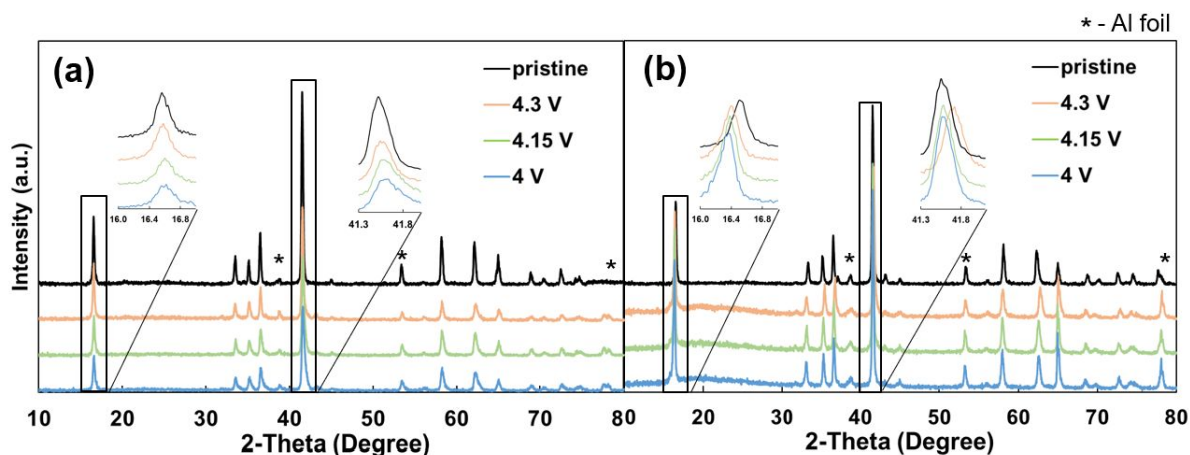
Figure S7. *Ex-situ* XRD performed on cathodes after (a) 20 cycles at 1C rate and (b) 50 cycles at 1C rate, compared to the pristine, uncycled cathode.
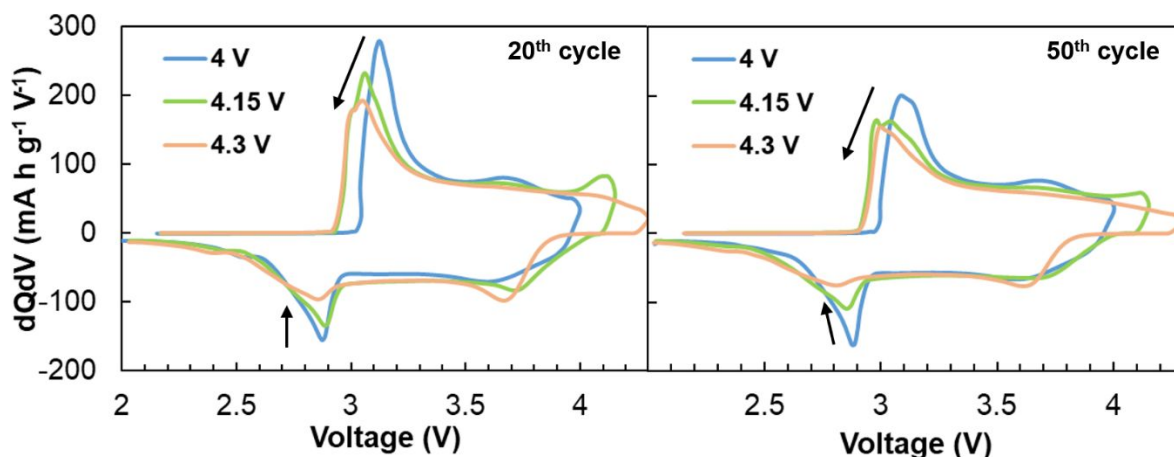
Figure S8. dQ/dV plot of the 20th and 50th cycles of cells cycled at C/5 rate to varying voltages, showing a decrease in the lower voltage O3 to P3 phase transition. Data were averaged for reduced noise.

Table S1. Equivalent circuit used for fitting EIS curves and resistance values of each semi-cirle with standard deviation. R2 corresponds to R_f and R4 to R_{ct}.
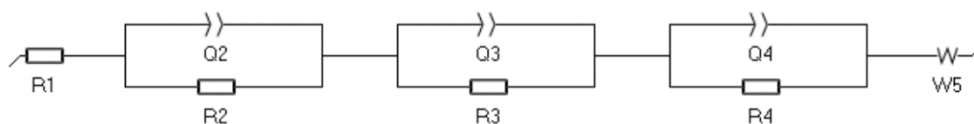
		4 V		
	R2	R3	R4	S.D.
1st cycle	4.6	31.7	157.1	0.6
5th cycle	6.2	28.2	188.3	0.4
20th cycle	7.8	22.4	132.9	0.7
		4.15 V		

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	R2	R3	R4	S.D.
1st cycle	7.0	38.9	122.9	2.9
5th cycle	10.5	31.3	141.4	0.6
20th cycle	12.9	27.5	171.5	0.6

	4.3 V			
	R2	R3	R4	S.D.
1st cycle	6.8	32.4	120.2	0.6
5th cycle	8.7	30.4	162.4	0.6
20th cycle	13.8	23.4	237.4	0.6

Table S2. Lattice constants and volume per formula unit of each phase, showing the expansion and contraction that occurs during cycling.

	a	c	V per formula unit
Discharged state (O3 phase)	16.09477	2.977232	41.18
4 V (P3 phase)	16.931	2.9214	41.71
change from O3	5.2%	-1.9%	1.3%
4.3 V (OP2 phase)	10.61	2.895	38.50
change from P3	-6.0%	-0.9%	-7.7%

Table S3. The total capacity contribution (mA h g^{-1}) of the P3 to OP2 phase transition at cycle numbers 1, 2, 5, and 10 on cells charged up to 4.15 and 4.3 V. Calculated by measuring the area under the corresponding peak in the dQ/dV plot relative to any non-peak area above 4 V. Total charge capacity at each cycle is given for reference.

	Capacity Contribution Above 4 V - 4.15 V			
Cycle #	Total Charge	OP2 Peak	Background	Sum
1st	141	16	10	26
2nd	128	12	8	21
5th	122	7	8	16
10th	118	5	9	14

	Capacity Contribution Above 4 V - 4.3 V			
Cycle #	Total Charge	OP2 Peak	Background	Sum
1st	149	16	20	36
2nd	133	8	18	26
5th	125	4	18	21
10th	117	1	16	17