Electronic Supplementary Information (ESI)

Electrochemical properties and structural evolution of O3-type layered sodium mixed transition metal oxides with trivalent nickel

Plousia Vassilaras,[a] Deok-Hwang Kwon,[b] Stephen Dacek,[a] Tan Shi,[b] Dong-Hwa Seo,[b] Gerbrand Ceder,[a,b,c] and Jae Chul Kim[c,*]

[a]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
[b]*Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California 94720*
[c]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Table S1. Lattice parameters of $NaNi_{0.5}Co_{0.5}O_2$ and $NaNi_{0.5}Fe_{0.5}O_2$ obtained from Rietveld refinement using C2/m symmetry. c_h is derived from refinement with $R\bar{3}m$ symmetry.

Composition	a_m (Å)	b_m (Å)	c_m (Å)	β (°)	a_m / b_m	c_m 3sinβ (Å)	c_h (Å)
$NaNi_{0.5}Co_{0.5}O_2$	5.0580(2)	2.9130(2)	5.4774(2)	107.93(7)	1.736	15.6342	15.6441
$NaNi_{0.5}Fe_{0.5}O_2$	5.1776(2)	2.9882(1)	5.5792(2)	107.918(2)	1.733	15.9256	15.9236

Table S2. a_m to b_m ratio of $Na_{1-x}Ni_{0.5}Co_{0.5}O_2$ obtained from Rietveld refinement using the C2/m symmetry. (Site occupancy, atomic coordination, and B-factors are not refined.)

x in $Na_{1-x}Ni_{0.5}Co_{0.5}O_2$	a_m (Å)	b_m (Å)	a_m / b_m	*Symmetry*
0.15	4.9140	2.8849	1.703	C2/m (O'3)
0.30	4.9032	2.8238	1.755	C2/m (P'3)
0.38	4.8769	2.8179	1.730	$R\bar{3}m$ (P3)
0.49	4.8805	2.8000	1.743	C/2m (P"3)
0.63	5.3450	2.7998	1.909	C/2m (O"3)

Table S3. Lattice parameters of $Na_{1-x}Ni_{0.5}Fe_{0.5}O_2$ obtained from Rietveld refinement using the C2/m symmetry. (Site occupancy, atomic coordination, and B-factors are not refined.)

x in $Na_{1-x}Ni_{0.5}Fe_{0.5}O_2$	a_m (Å)	b_m (Å)	c_m (Å)	β (°)	a_m / b_m	c_m 3sinβ (Å)	c_h (Å)
0.17	5.111(3)	2.965(2)	5.644(3)	107.54(7)	1.738	16.1131	16.112(8)
0.49	4.978(1)	2.887(9)	5.870(1)	106.46(4)	1.737	16.986	16.987(7)

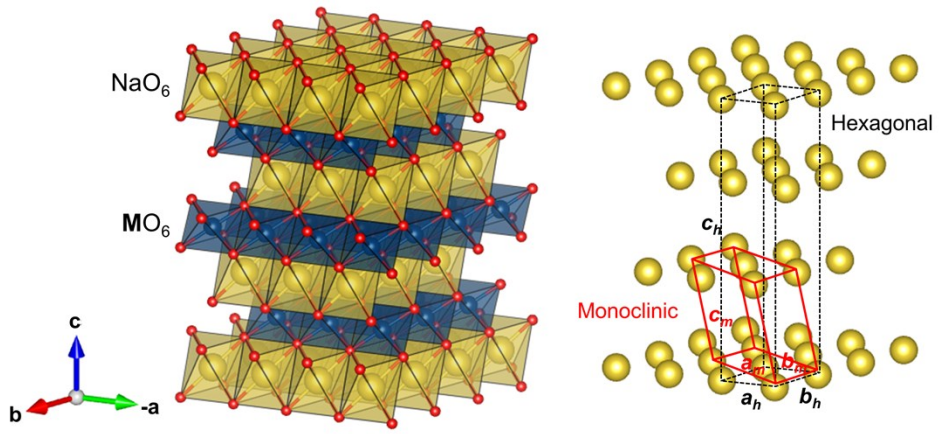

Figure S1. Hexagonal ($R\bar{3}m$) and monoclinic (C2/m) unit cells in O3-type layered rock-salt structure.

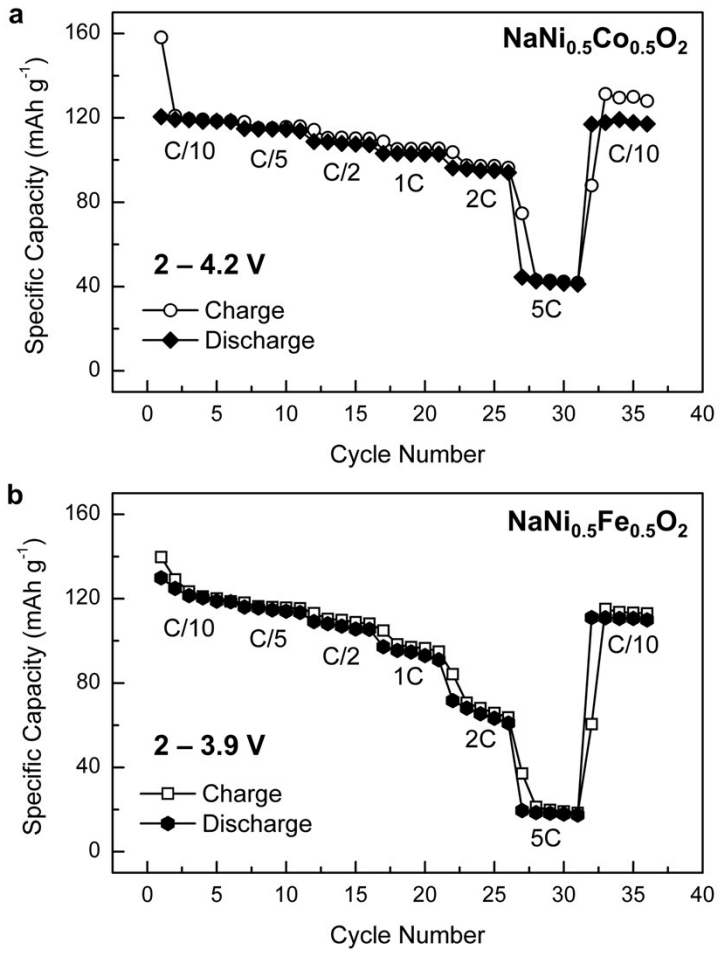

Figure S2. Charge and discharge capacities of (a) $NaNi_{0.5}Co_{0.5}O_2$ and $NaNi_{0.5}Fe_{0.5}O_2$ at various rates at RT

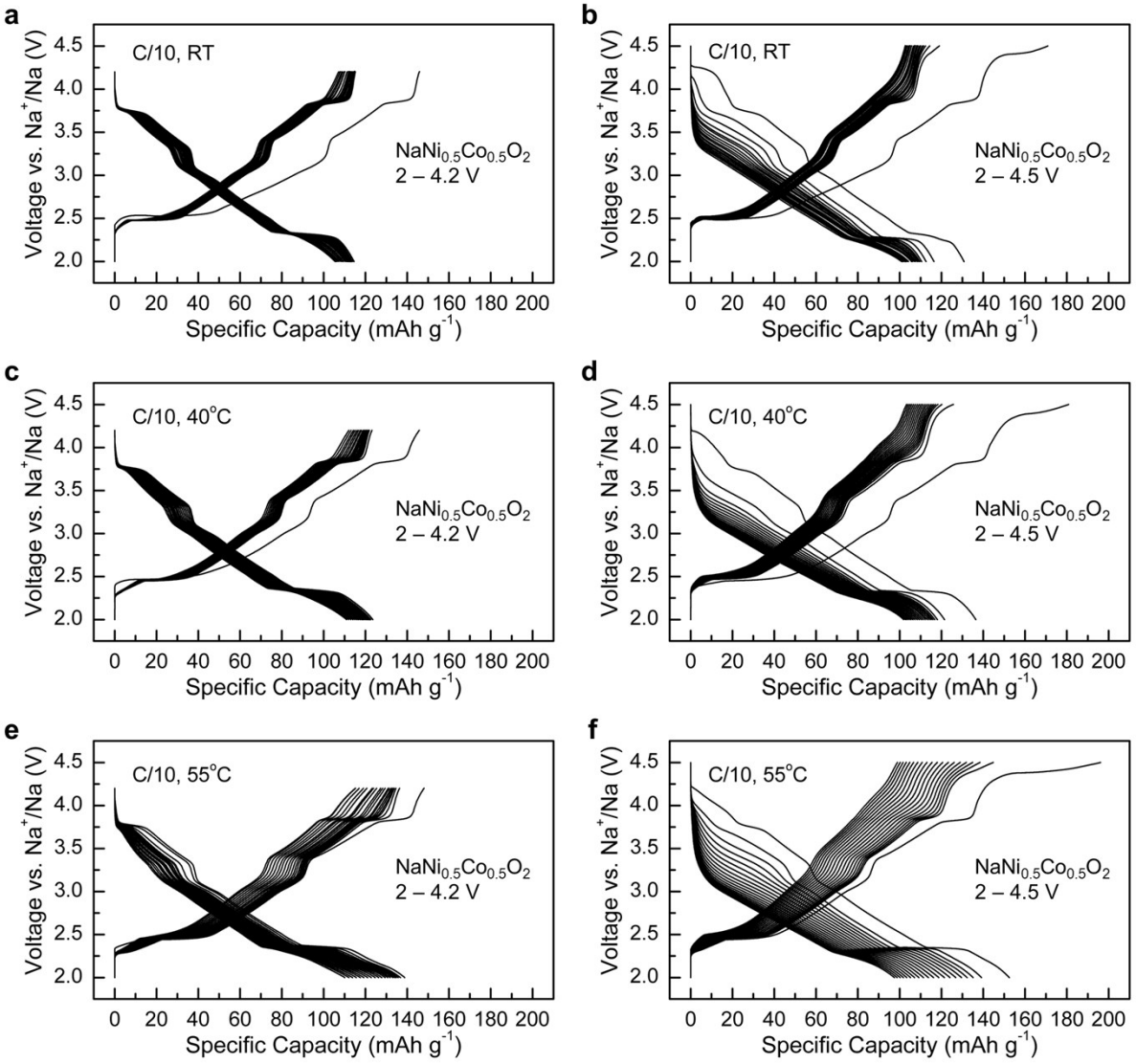

Figure S3. Voltage profiles of $NaNi_{0.5}Co_{0.5}O_2$ with respect to specific capacity in various conditions (20 cycles)

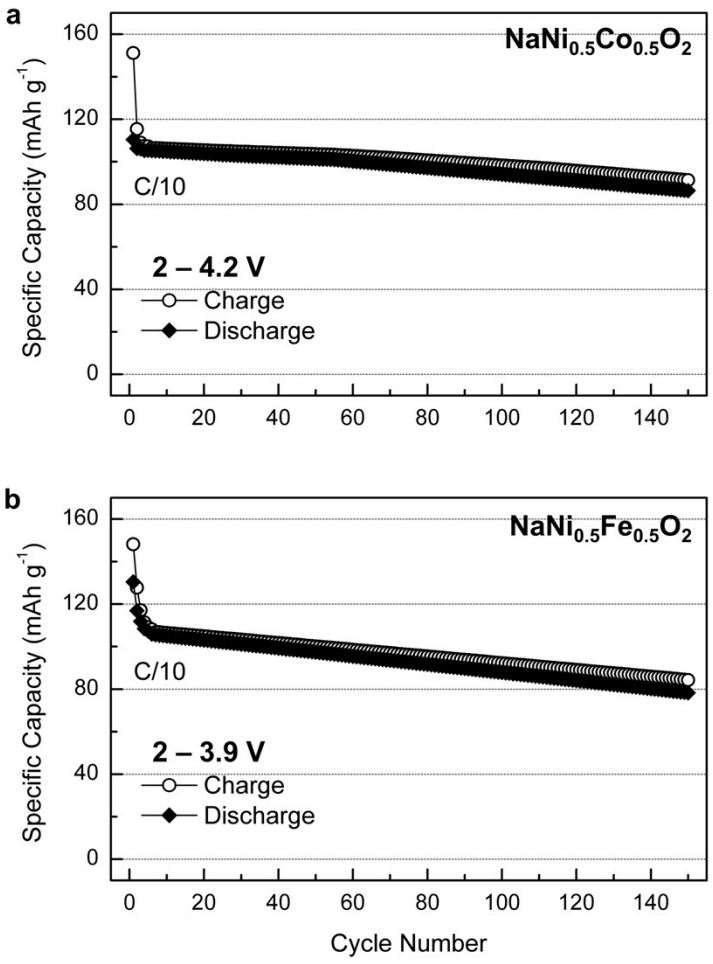

Figure S4. Charge and discharge capacities of (a) $NaNi_{0.5}Co_{0.5}O_2$ and $NaNi_{0.5}Fe_{0.5}O_2$ at a C/10 rate at RT

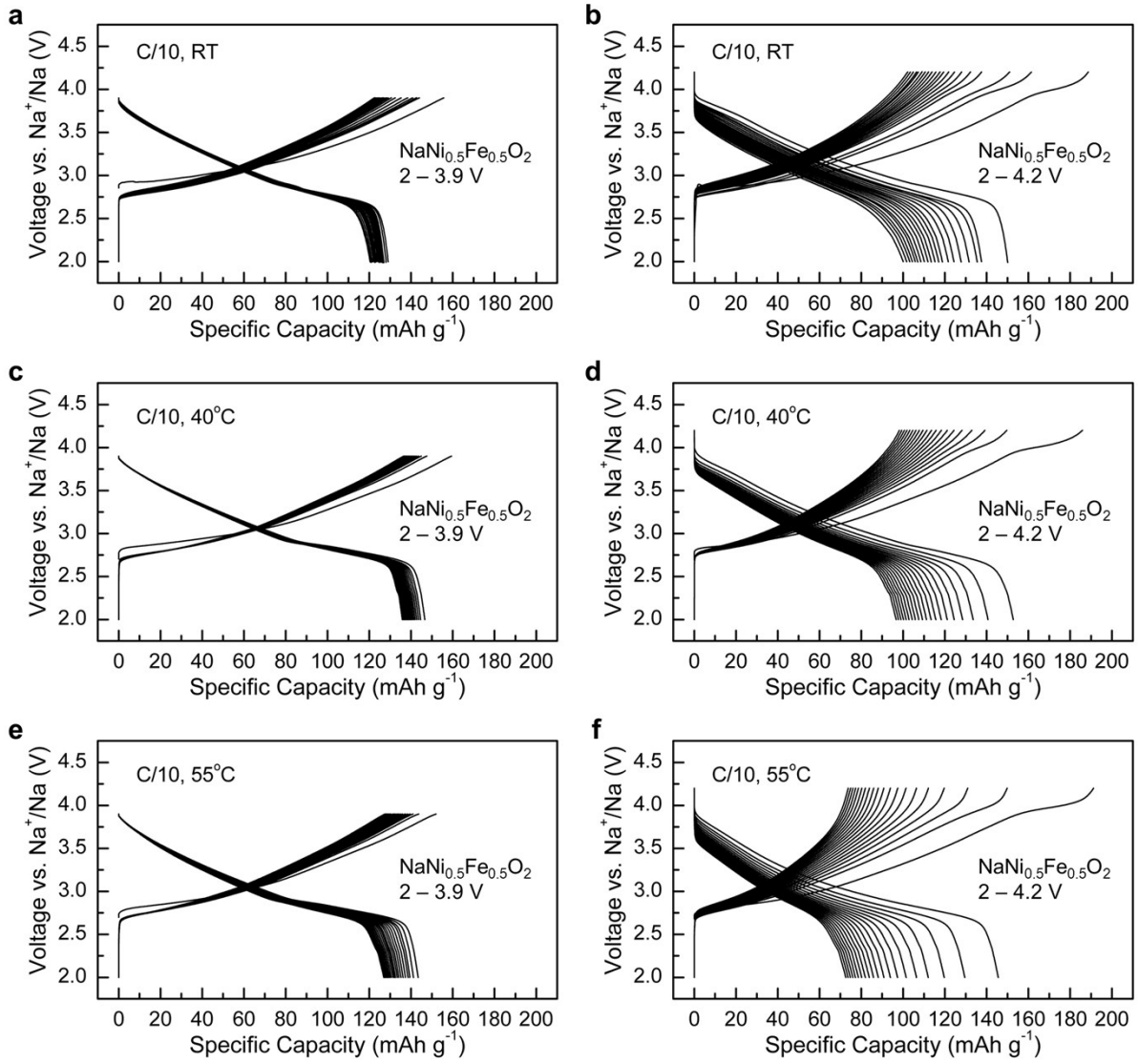

Figure S5. Voltage profiles of $NaNi_{0.5}Fe_{0.5}O_2$ with respect to specific capacity in various conditions (20 cycles)

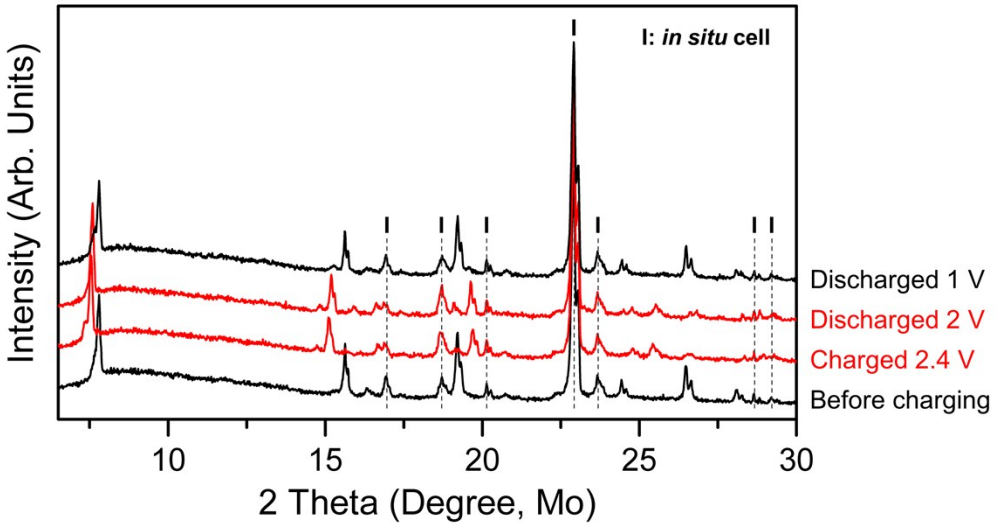

Figure S6. In situ XRD patterns obtained at different voltages during cycling. Tick marks indicate peaks from *in situ* cell components.

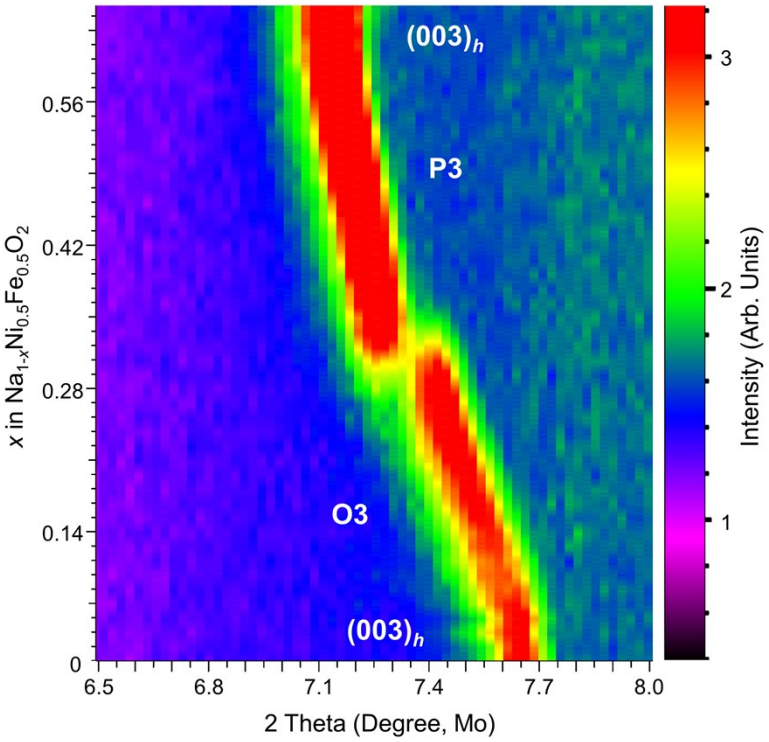

Figure S7. *In situ* XRD patterns of $NaNi_{0.5}Fe_{0.5}O_2$ around the $(003)_h$ peak.

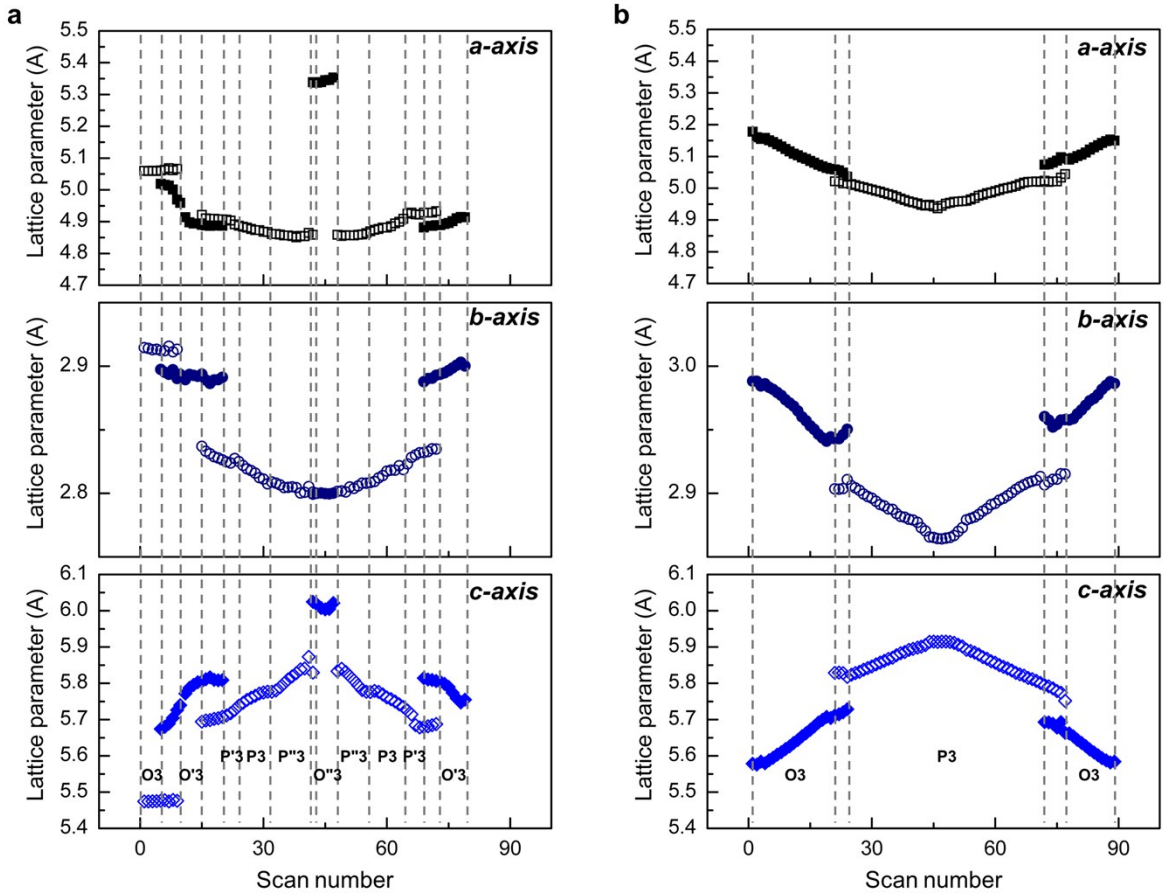

Figure S8. Lattice parameter evolution of (a) $Na_{1-x}Ni_{0.5}Co_{0.5}O_2$ and (b) $Na_{1-x}Ni_{0.5}Fe_{0.5}O_2$ in the first charge and discharge