Supporting Information

Suppression of Monoclinic Phase Transitions of O3-Type Cathodes Based on Electronic Delocalization for Na-Ion Batteries

Hu-Rong Yao,[†,‡,//] *Wei-Jun Lv,*[†,//] *Ya-Xia Yin,*[‡,⊥] *Huan Ye,*[‡] *Xiong-Wei Wu,*[‡] *Yi Wang,*[§,⊥] *Yue Gong,*[§,⊥] *Qinghao Li,*[§,⊥] *Xiqian Yu,*[§,⊥] *Lin Gu,*[§,⊥] *Zhigao Huang,*[*,†,//] *Yu-Guo Guo*[*,‡,⊥]

†Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials College of Physics and Energy, Fujian Normal University, Fuzhou 350117, China

‡CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China.

§Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

//Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China

⊥University of Chinese Academy of Sciences, Beijing 100049, China

*To whom correspondence should be addressed. E-mail address: ygguo@iccas.ac.cn (Y.-G. G.); zghuang@fjnu.edu.cn (Z.-G. H.).

EXPERIMENTAL SECTION

DFT calculations. To simulate the impacts of incorporated Fe^{3+} on crystal and electronic structure of $NaNi_{0.5}Mn_{0.5}O_2$, the DFT calculations were carried out with the projector augmented wave (PAW) methods utilized by the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) of Perdew−Burke−Ernzerhof with the GGA+U extension was used to describe electron exchange and correlation. The U value for Fe, Ni and Mn were 4.5, 6.1 and 4.0 eV respectively. All simulations used a plane wave energy cutoff of 520 eV, the Monkhorst-Pack scheme k-mesh was denser than 0.03 Å^{-1}. The relaxations were converged to within a force convergence criterion of 0.01 eV Å^{-1}. The $NaNi_{0.5}Mn_{0.5}O_2$ structural model of 6a × 3b × 1c supercell containing 216 atoms was used. To simulate bulk structure of Fe dopant, nine of Ni and Mn ions were substituted with Fe ions respectively.

Synthesis. The $O3\text{-}NaFe_xNi_{0.5\text{-}x/2}Mn_{0.5\text{-}x/2}O_2$ (x = 0, 0.3) samples were easily prepared using solid-state reaction using Na_2CO_3 (Alfa Aesar, 99.5%), Fe_2O_3 (Alfa Aesar, 99.9%), NiO (Alfa Aesar, 99.0%) and Mn_2O_3 (Alfa Aesar, 98.0%). Firstly, the stoichiometric precursors (access 5mol% of Na_2CO_3) were ground in a mortar, then compacted at 10 MPa pressure load. The mixtures were calcined at 1000 °C for 15 h in air to obtain the target materials.

Characterizations. The morphologies were investigated through SEM measurements performed on JEOL 6701F apparatus operated at 10 kV and EDS measurement using JEM 2100F equipment. The XRD profiles were collected on Bruker D8 advance diffractometer with Cu Kα radiation and the crystal structures of samples were carried out using TOPAS software.

The in-situ XRD patterns were obtained equipped with a special battery using Al foil as current collector and window for X-ray. The ABF-STEM images was executed with a JEM-ARM200CF (JEOL, Tokyo, Japan) equipped with cold emission gun and double hexapole Cs corrector (CEOS GmbH, Heidelberg, Germany), operated at 200 kV.

Electrochemistry. The electrochemical performances were obtained with Na half-cells. The working electrodes were fabricated by preparing the slurry with active material, Super P and poly(vinyl difluoride) (PVDF) in a mass ratio of 7:2:1 spread on Al current collector dried under vacuum for one night, and then cut into small rounds of 1 cm diameter. For assembling the coin-type cells, the electrodes were transferred into the Ar-filled glove box, and the used electrolyte was 1 M $NaClO_4$ in propylene carbonate (PC, 5% FEC). The galvanostatic charge/discharge profiles were obtained on Land BT2000 within 2.0–4.0 V voltage range. The results of CV measurement were collected on an Autolab PG302N equipment. The apparent diffusion coefficient can be calculated from the $\nu^{1/2}$–dependent I_p function.

$$I_P = 0.4463 n^{3/2} F^{3/2} C S R^{-1/2} T^{-1/2} D^{1/2} \nu^{1/2}$$

Where I_p is peak current, n is charge transfer number during the reaction, F is the Faraday constant, C is the Na^+ concentration extracted from electrodes, S is electrode area, R is the gas constant, T is absolute temperature, D is Na^+ apparent diffusion coefficient, ν is scan rate.
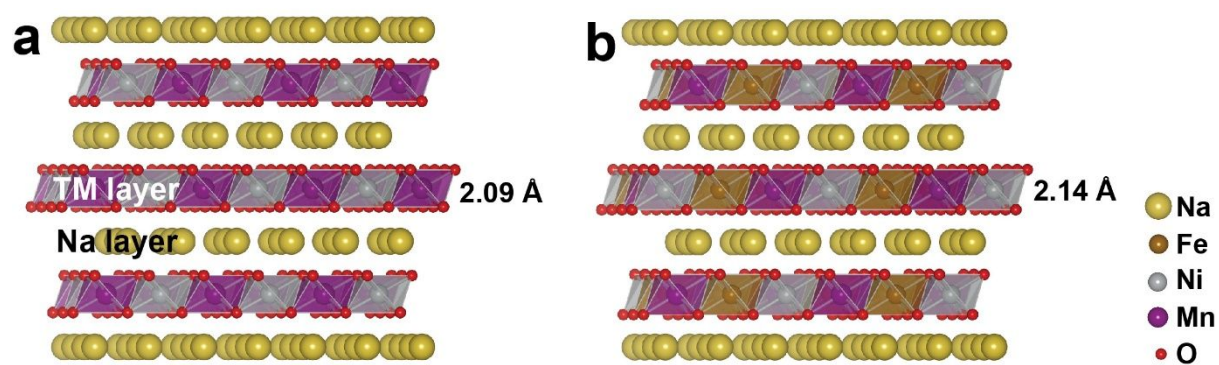
Figure S1. Calculated crystal structures of (a) $NaNi_{0.5}Mn_{0.5}O_2$ and (b) $NaFe_{0.3}Ni_{0.35}Mn_{0.35}O_2$.

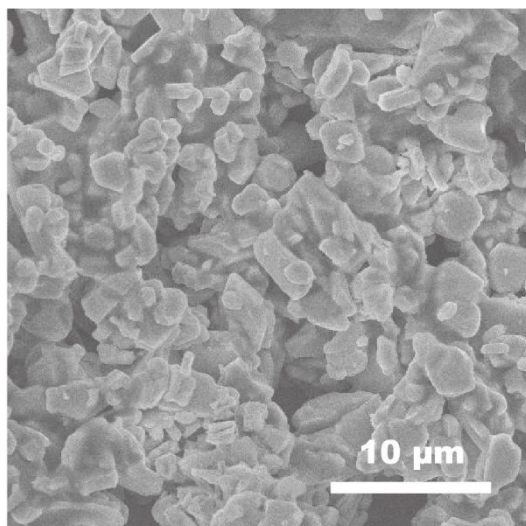**Figure S2.** (a) SEM image of $NaFe_{0.3}Ni_{0.35}Mn_{0.35}O_2$.
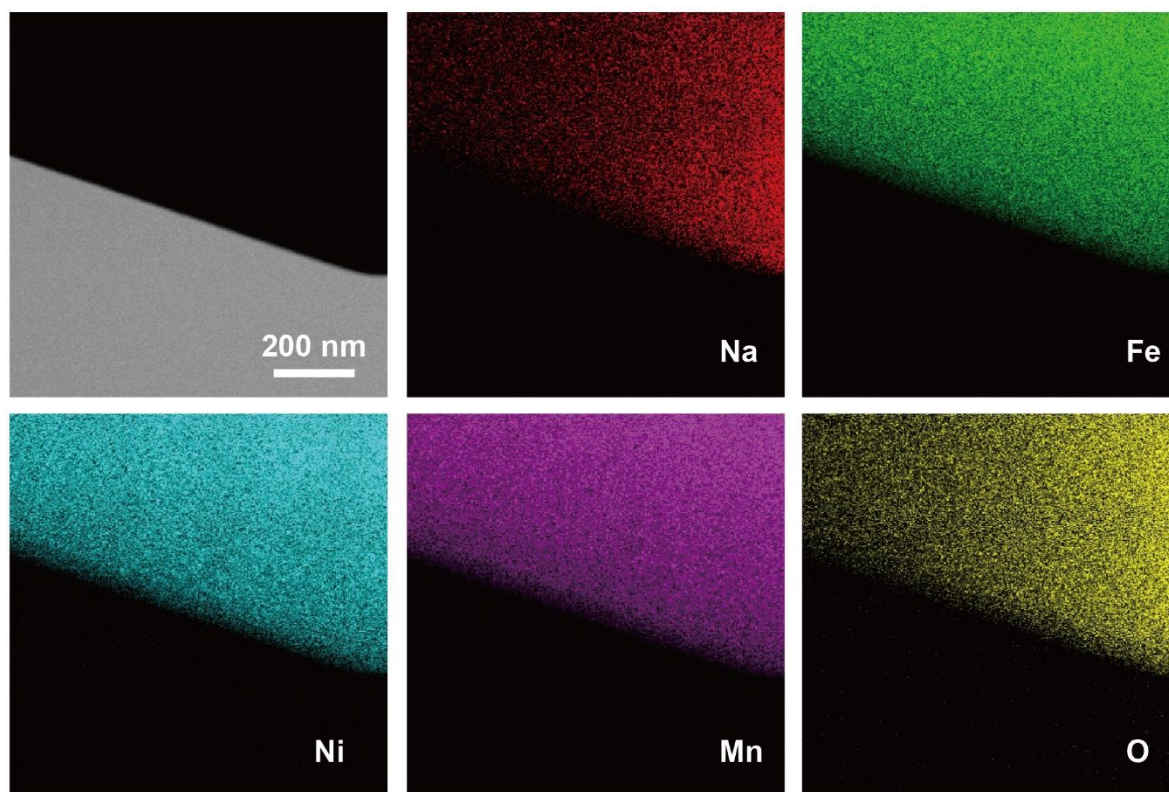
Figure S3. EDS analysis for $NaFe_{0.3}Ni_{0.35}Mn_{0.35}O_2$.

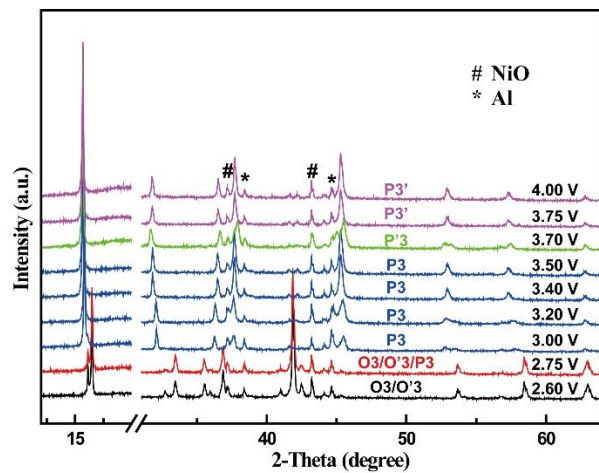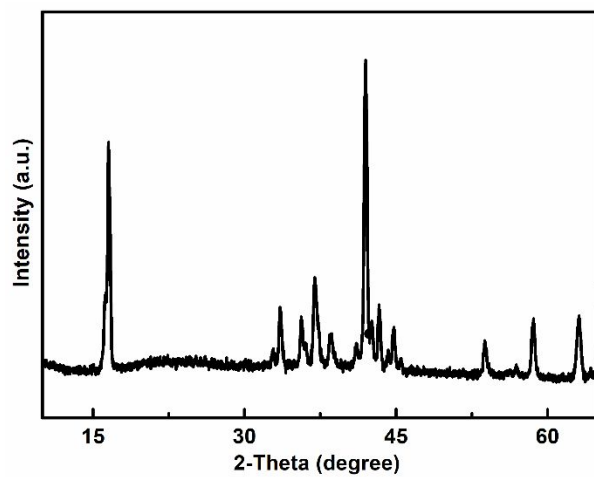**Figure S4**. The ex-situ XRD patterns of NaNi$_{0.5}$Mn$_{0.5}$O$_2$ electrodes at various charge states.

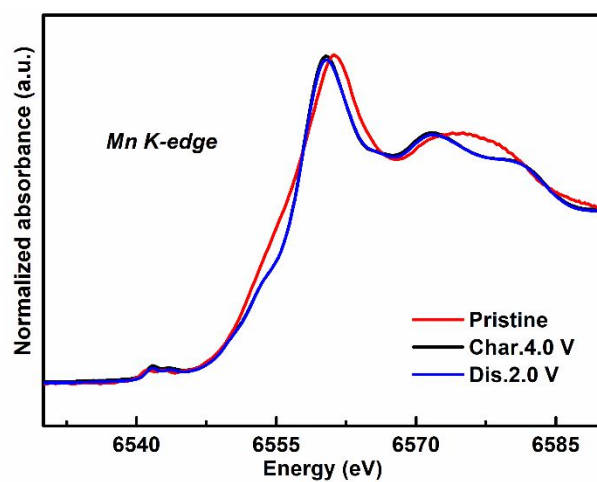**Figure S5**. The XRD pattern of $NaNi_{0.5}Mn_{0.5}O_2$ electrode after cycled 10 times.

Figure S6. XANES data at the Mn *K*-edge of $NaFe_{0.3}Ni_{0.35}Mn_{0.35}O_2$ recorded under various electrochemical states.

Table S1. Refined crystallographic parameters of O3- $NaNi_{0.5}Mn_{0.5}O_2$.

Space group	R-3m (No. 166)				
Atom	site	x	y	z	occ
Na	3a	0	0	0	1.00
Ni	3b	0	0	0.5	0.50
Mn	3b	0	0	0.5	0.50
O	6c	0	0	0.2249	1.00
a = 2.9481(8) Å	c = 16.0497(7) Å	R_p = 5.10%	R_{wp} = 6.99%	(NiO)Wt% = 7.5%	

Table S2. Refined crystallographic parameters of O3- $NaFe_{0.3}Ni_{0.35}Mn_{0.35}O_2$.

Space group	R-3m (No. 166)				
Atom	site	x	y	z	occ
Na	3a	0	0	0	1.00
Fe	3b	0	0	0.5	0.30
Ni	3b	0	0	0.5	0.35
Mn	3b	0	0	0.5	0.35
O	6c	0	0	0.2303	1.00
a = 2.9787(0) Å	c = 16.0094(0) Å	R_p = 5.35%	R_{wp} = 7.03%	(NiO)Wt% = 1.2%	