Supporting Information

Revealing High Na-Content P2-Type Layered Oxides as Advanced Sodium-

Ion Cathodes

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Methods

Sample synthesis.

The resulting materials, $Na_{45/54}Li_{4/54}Ni_{16/54}Mn_{34/54}O_2$ and $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ were prepared by a solidstate reaction. The stoichiometric precursors of $NaNO_3$ (>98%), NiO (>98%), MnO_2 (99%) and Li_2CO_3 (99.5%) were thoroughly mixed in an agate mortar and pressed into pellets under pressure of 10 MPa, which was further calcined at 950-1050 °C for 24 h with an intermediate grinding and cooled to room temperature naturally. More 5% NaNO₃ and 2% Li_2CO_3 were used for the volatilization loss at high temperature. After the heat treatment, the material was directly put into an Ar-filled glovebox to prevent any moisture exposition. Hard carbon anode was prepared according to our previous report¹, where the obtained samples were carbonized at 1400 °C for 3 h in a tube furnace under argon flow with a heating rate of 3°C min⁻¹.

Materials characterizations.

Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source (λ_1 =1.54060 Å, λ_2 =1.54439 Å) and a LynxEye XE detector. Rietveld refinement of the XRD was carried out using the General structure analysis system (GSAS) software with the EXPGUI software interface.² High-resolution transmission electron microscopy (HR-TEM) images and scanning transmission electron microscopy (STEM) image and electron energy loss spectroscopy (EELS) mappings were obtained using a 300 kV aberration-corrected (S)TEM (JEM-ARM300F, JEOL Ltd) operated at 300kV with a cold field-emission gun and double dodeca-poles Cs correctors. The convergence angle was 18mrad and the angular range of collected electrons for highangle annular dark field (HAADF) imaging is about 54-220 mrad. The morphologies of the materials were investigated using a scanning electron microscope (SEM) (Hitachi S-4800). The stoichiometry of the as-synthesized compound was determined measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). In the *in-situ* XRD studies, the working electrode was prepared using PVDF as binder on an Al foil. A specially designed Swagelok cell equipped with an X-ray transparent Al window was used for the *in-situ* measurements on charge and discharge. Mn/NiL-edge and O K-edge X-ray absorption spectroscopy (XAS) were performed for pristine and cycled samples in the electron (surface) and fluorescence yield (bulk) modes at beamline 4-ID-C of the Advanced Photon Source. Samples were transferred from a glovebox into a transfer container and then an X-ray absorption chamber via an argon environment. This was done in order to maintain a clean sample. During the measurement, Sr₂RuO₄, MnO and Ni metal were used as standards for the energy calibration of O K-edge, Mn L-edge and Ni L-edge, respectively. The X-ray adsorption near edge spectroscopy (XANES) spectra of Mn K-edge were collected at P64 beamline, DESY, Hamburg, Germany. The transmission spectra were measured and monochromatized by a Si(111) double-crystal monochromator. The spectra were processed using the Athena software package.³

Electrochemical measurement.

The cathodes were prepared *via* mixing 80 *wt*.% active material with 10 *wt*. % acetylene black and 10 *wt*. % polyvinylidene fluoride (PVdF) on Al foil with the loading mass of the active material was about $8 \sim 10 \text{ mg cm}^{-2}$. The anodes were prepared via mixing 80 *wt*.% active material with 10 *wt*.% conductive additives (acetylene black: super P = 8:2) and 10 *wt*.% sodium alginate binder on Cu foil with the loading mass of the active material was $1.6 \sim 2 \text{ mg cm}^{-2}$. The prepared electrodes were dried at 100 °C under vacuum for 12 h and then were fabricated into CR2032 coin-type cells with pure sodium foil as the counter electrode in an argon-filled glove box (H₂O, O₂ < 0.1 ppm). A glass fiber was used as the separator, and 0.2 M NaPF₆ and 0.8 M NaClO₄ in ethylene carbonate/diethyl carbonate (EC/DEC =

4:6 in volume) with fluoroethylene carbonate (5% in volume) was used as the electrolyte. The charge and discharge measurements were carried out on a Land BT2000 battery test system (Wuhan, China) under room temperature.

Accelerated aging measurement.

In order to check the water stabilities of the electrode materials, the as-synthesized materials were first placed in deionized water with pH values of 7 for 2 h. Then, the materials were separated from the solution and dried in an oven at 100 °C for overnight. Note that this is an extreme condition which will never be happened for practical materials process. However, this result can reflect the stability of the material against water in a short time.

Computational methods. All first-principles DFT calculations reported in this study were performed using the Vienna Ab-initio Simulation Package (VASP)⁴⁶ with the projector augmented wave (PAW) potentials⁷ and the Perdew-Becke-Ernzerhof (PBE)⁸ exchange-correlation. A plane wave basis with a cutoff energy of 520 eV and Γ -centered *k*-meshes with a density of 8000 *k*-points per reciprocal atom were used for all calculations. All calculations were spin-polarized, with Mn atoms initialized in a high-spin configuration and relaxed to self-consistency with the ferromagnetic (FM) configurations applied. The DFT + *U* method introduced by Dudarev *et al.*⁹ was used to treat the localized 3*d* electrons of Mn, Ni with a *U* of 3.8 and 6.1 eV, obtained by fitting it to experimental and calculated formation enthalpies in a previous study¹⁰.

The average (de)sodiation voltage can be computed using the negative of the reaction free energy per Na added/removed, as shown

$$V = \frac{\Delta G_{\rm f}}{\rm F} \Delta N_{\rm Na}$$

where F is the Faraday constant, ΔN_{Na} is the amount of Na added/removed, and ΔG_{f} is the (molar) change in free energy of the reaction. Considering a two-phase reaction between Na_xTMO and Na_yTMO, Na_xTMO + $(y - x)Na \rightarrow \text{Na}_{y}\text{TMO}$, ΔG_{f} can be approximated by the total internal energies from DFT calculations neglecting the entropic contributions (T = 0 K)

 $\Delta E = E(\text{Na}_{x}\text{TMO}) - E(\text{Na}_{y}\text{TMO}) - (y - x)E(\text{Na}_{\text{metal}})$

where $E(Na_xTMO)$ and $E(Na_yTMO)$ are the DFT energies at the respective compositions. The neglect of entropic contributions means that the lithiation voltage profiles will follow the T = 0 K ground-state convex hull and consist of a series of constant voltage steps along the two-phase regions of the convex hull, separated by discontinuities that indicate the single-phase compounds on the hull. It is worth mentioning here that, in practice, (de)sodiation do not necessarily proceed through two-phase reactions. Thus, the calculated T = 0 K voltage profiles should be viewed as an approximation to the actual voltage profiles¹¹. At finite temperatures (for example, room temperature), the "steps" in the voltage profile became more rounded because of entropic effects⁴.

The first-principles molecular dynamics (FPMD) calculations is used to investigate the Na ions transport properties in this high Na-content P2-type oxide. This FPMD simulations are carried out for 10 ps at each temperature by a Nose-Hoover thermostat, and a time step of 1 fs is used to integrate the equation of motion, where the Γ point is used for the Brillouin zone in order to keep the computational cost at a reasonable level. The ionic diffusion behavior in this system is calculated by a time-dependent mean square displacement (MSD),

$$MSD(t) = \langle r^2(t) \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle$$

where $r_i(t)$ is the position of the *i*-th Na⁺ at the time *t*, and the average is over the time steps and all the Na⁺. According to the Einstein equation, the slope of the MSD presents the diffusion coefficient D,

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle r^2(t) \rangle$$

therefore, the activation energy barrier for Na⁺ diffusion can be extracted from the diffusion coefficients at various temperatures according to Arrhenius equation.

Supporting discussion

S1. Determination of the Li/Ni/Mn (dis)ordering in the system of Na_{1-x}Li_{1/12}Ni_{1/4}Mn_{2/3}O₂.

The lowest-energy, ground state structure of Na_{1%}Li_{1/12}Ni_{1/4}Mn_{2/3}O₂ is determined by a vast number of geometrically-distinct Na/Vac and Li/Ni/Mn ordered configurations using density functional theory (DFT) calculation based (nonequilibrium phase searching method) NEPS method¹²⁻¹³. Starting from the partially-occupied structure from the XRD refinement, which has Na/vacancy sharing the Na sites and Li/Ni/Mn sharing the metal sites, we generate supercells containing 12 Na sites and 12 metal sites. We then populate the metal sites with Li, Ni and Mn in the ratio 1:3:8, and introduce Vac to substitue Na. Total 910 geometrically different configurations were generated using the Enum code¹⁴⁻¹⁶. We calculated the electrostatic total energy for all configurations using nominal charge states for the ions in the system as a quick energy sampling step¹⁷. All structures were ranked by their normalized electrostatic energies, and the 100 NaLi_{1/12}Ni_{1/4}Mn_{2/3}O₂ structures with the lowest electrostatic energies were fully relaxed, and their energies calculated, using DFT. We find the structure with the lowest DFT total energy, *i.e.*, the ground state structure of NaLi_{1/12}Ni_{1/4}Mn_{2/3}O₂, has a space group of *C2/m*. The total energies of all geometrically distinct structures were calculated using DFT, and select the configuration with the lowest DFT total energy.

S2. Structural evolution at different rates.

Considering that this structural evolution is related to the Na concentration in host structure, thus, the different charged rates will induce the different behaviours resulting from the uneven Na distribution in the materials. *In-situ* XRD experiments on a ten-times higher rate density were carried out shown in Supporting Information Figure S17. Compared to the low current density, the phase evolution at a higher current rate is delayed and the fractions of Na-poor phase 2 and phase 3 have changed. At low rate, the Na-poor phases are found to appear at the very beginning of the charge process, and the Na-poor phase 3 dominated the following process. While at high rate, these Na-poor phases appear with more Na deintercalation from the pristine structure in the middle of the charge process. Compared to the dominant behaviour of phase 3, the phase 2 plays a more key role in this high current density. These Na-poor phase 2 and phase 3 can be defined as the intermediate phases in the desodiation process, in which phase 3 is more stable. In a fast charge process, Na⁺ can't reach a rapid equilibrium state along with the Na⁺ diffusion, leading to the formation of intermediates. More

interestingly, this behaviour differs from the previous reports of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and LiFePO₄ materials in Li-ion batteries¹⁸⁻¹⁹, where the intermediate phases in different structures are produced. In this high Na-content material, only the same P2 phases appear. More importantly, no matter which intermediate phase is dominant in this structure, they always contribute to a positive effect on the properties of this P2 material due to their larger interlayer distance than that of the pristine phase, while these structures of newly formed intermediate phases remain unchanged until to the further desodiation state. Compared to the complex behaviours in Li-ion systems, it is unveiled that this structural change behaviour can provide the better advantage for ion migration due to its enough Na in the host.



Figure S1. Crystal structure of the O3- and P2-type oxides. a. O3-type oxide in the Rhombohedral structure with the space group of R-3m (166) and b. P2-type oxide in the hexagonal structure with the space group of $P6_3/mmc$ (194). Vac is vacancy; and TM is transition metal.



Figure S2. Electrochemical performance of typical P2-type and O3-type Na-ion cathodes. a. TM^{2+} -based cathodes, including the Ni²⁺ or Cu²⁺, usually show the high voltage more than 3.2 V; TM^{3+} -based cathodes, including the Mn³⁺ or Co³⁺, usually deliver the high capacity of >100 mAh g⁻¹ below 4.0 V. b. O3-type cathodes usually deliver the high capacity of > 100 mAh g⁻¹ below 4.0 V, but with the low voltage.



Figure S3. Scanning electron microscope (SEM) image of this high Na-content P2-type $Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O_2$ compound.



 $\label{eq:Figure S4. High-resolution transmission electron microscope (HRTEM) image of this high Nacontent P2-type Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O_2 \ compound.$



Figure S5. Evaluation the stability of the $Na_{5/6}Li_{1/12}Ni_{1/4}Mn_{2/3}O_2$ phase in the Na-Li-Ni-Mn-O chemical space.

According to the Open Quantum Materials Database (OQMD) framework²⁰⁻²¹, the known stable phase combination at the $Na_{5/6}Li_{1/12}Ni_{1/4}Mn_{2/3}O_2$ stoichiometry is:

 $3/8NaMnO_2 + 1/24Li_2MnO_3 + 1/12\ Na_2Mn_3O_7 + 1/24Na_2O_2 + 1/4NaNiO_2$ As identified Na_{5/6}Li_{1/12}Ni_{1/4}Mn_{2/3}O₂ exhibit even lower energy: -1.68 eV/atom.



Figure S6. Cycling stability of $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ with first three cycles at 0.1C and following at 3.0C in the voltage ranges of 2.0-4.0 V vs. Na^+/Na .



Figure S7. Cycling stability of $Na_{45/54}Li_{4/54}Ni_{16/54}Mn_{34/54}O_2$ with first three cycles at 0.1C and following at 3.0C in the voltage ranges of 2.0-4.0 V vs. Na^+/Na .



Figure S8. The magnetization and oxidation state evolution during the desodiation process of Mn ions in intermediate phases from $Na_{5/6}Li_{1/12}Ni_{1/4}Mn_{2/3}O_2$ to $Li_{1/12}Ni_{1/4}Mn_{2/3}O_2$.



Figure S9. Ni *L*-edge X-ray absorption spectra (XAS) of electrochemically cycled Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O₂ electrodes in partial fluorescence yield (PFY) mode.



Figure S10. O *K*-edge XAS spectra of electrodes cycled to different states of charge (SOCs) using (a) PFY mode and (b) total electron yield (TEY) mode.



Figure S11. Ni and Mn *L*-edge XAS spectra of electrodes cycled to different SOCs using TEY mode.



Figure S12. Mn L-edge XAS spectra of electrodes cycled to different SOCs using PFY mode.



Figure S13. X-ray absorption near edge spectroscopy (XANES) spectra of the Mn *K*-edge at different states of charge and the standard Mn-based oxides with Mn^{2+} , Mn^{3+} and Mn^{4+} .



Figure S14. XRD Rietveld refinement of the electrochemically oxidized Na_{~0.25} Ni_{16/54}Mn_{34/54}Li_{4/54}O₂ sample. Three P2 phases are indexed in hexagonal *P*6₃/*mmc* symmetry with the fractions of 5.1(2)%, 32.3(2)%, 62.6(2)%, respectively, corresponding to lattice parameters of a = 2.878(33) Å and c = 11.21(13) Å, a = 2.8668(4) Å and c = 11.2335(15) Å, a = 2.8135(13) Å and c = 11.2763(14) Å.



Figure S15. LeBail refinements of *in-situ* XRD patterns at different charge-discharge states of pristine, charged to 4.0 V, and discharged to 2.0 V.



Figure S16. Rietveld refinement of *ex-situ* X-ray diffraction (XRD) pattern of Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O₂ (a = 2.87831(19) Å, c = 11.1629(11) Å) after 100 cycles, and the inset showing the enlarged pattern of (002) peak. This compound is indexed in the hexagonal structure with the space group of *P*6₃/*mmc* (194).



Figure S17. Structural evolution under electrochemical Na^+ deintercalation to 4.0 V under different charged rates. **a** 0.05C and **b** 0.5C.



Figure S18. Mean square displacement (MSD) curves for each kind of ions in $Na_{5/6}Li_{1/12}Ni_{1/4}Mn_{2/3}O_2$. The MSD curves were simulated in temperature of 600 K, 1000 K, 1400 K, and 1800 K for 10 ps.



Figure S19. XRD patterns of the samples after stored half of a year **a** and soaked in neutral water for 2h **b**. The soaked materials were separated from the solution and dried in an oven at 100 °C for overnight.



Figure S20. Electrochemical performance of high Na-content P2 type cathode after soaked in neutral water for 2h. **a**, Galvanostatic charge-discharge curves at a rate of 0.15C in the voltage range of 2.0 and 4.0 V *vs.* Na⁺/Na. **b**, Cycling stability at a rate of 0.15C in the voltage range of 2.0 to 4.0 V.



Figure S21. Electrochemical performance of hard carbon anode. Galvanostatic chargedischarge curves at a rate of 0.1C in the voltage range of 0 and 2.5 V vs. Na⁺/Na. Cycling stability at a rate of 0.1 C in the voltage range of 0 and 2.5 V.



Figure S22. Galvanostatic charge-discharge curves of high Na-content P2-type cathode $Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O_2//hard carbon full cells. The first cycle is in the voltage range of 1.5-4.2 V, and the following cycles are in the 1.5-4.0 V.$



Figure S23. Cycling stability of high Na-content P2-type cathode $Na_{45/54}Ni_{16/54}Mn_{34/54}Li_{4/54}O_2//hard carbon full cells. The first two cycles are at the current rate of 0.1C, and the further cycles are at 2.5C.$

Table S1. Stoichiometry from the inductively coupled plasma atomic emission spectrometry

 (ICP-AES) analysis.

	Na	Mn	Ni	Li	Composition
$Na_{54/54}Li_{4/54}Ni_{16/54}Mn_{34/54}O_2$	0.8501	0.6192	0.3024	0.0792	$Na_{0.85}Li_{0.08}Ni_{0.30}Mn_{0.62}O_2$

Space group	P6 ₃ /mmc (194) - hexagonal		
Wavelengths	1.5406 Å		
Temperature	~300 K		
	a = b = 2.89058(7) Å,		
	c = 11.07541(18) Å		
Cell parameters	$\alpha = \beta = 90^\circ, \ \gamma = 120^\circ$		
	$V = 80.1420(30) \text{ Å}^3,$		
	Z = 4		
Reliability factors	$R_{wp} = 6.82\%$		
	$R_p = 5.19\%$		
	<i>Gof</i> = 1.61		
	$R_F^2 = 5.71\%$		

Table S2. Crystallographic and Rietveld refinement data of the as-prepared $Na_{54/54}Li_{4/54}Ni_{16/54}Mn_{34/54}O_2$ compound.

	х	У	Ζ	Occupancy	$U_{ m iso}$	Wyckoff
Na1	0	0	1/4	0.313(2)	0.0362(3)	2b
Na2	1/3	2/3	3/4	0.536(2)	0.0554(3)	2 <i>d</i>
Mn	0	0	0	0.621(1)	0.0913(1)	2 <i>a</i>
Ni	0	0	0	0.282(1)	0.0913(1)	2 <i>a</i>
Li	0	0	0	0.082(1)	0.0913(1)	2a
0	1/3	2/3	0.0873(1)	1.0	0.0901(3)	4 <i>f</i>

Table S3. Atomic coordinates, occupancies and isotropic displacement parameters (Å²).

	Phase 1	Phase 2	Phase 3		
Space group	P6 ₃ /mmc (194) - hexagonal				
Wavelengths	1.5406 Å				
Temperature	~300 K				
	a = b = 2.878(33) Å,	a = b = 2.8668(4) Å,	a = b = 2.8135(13) Å,		
	c = 11.21(13) Å,	<i>c</i> = 11.2335(15) Å,	<i>c</i> = 11.2763(14) Å,		
Cell parameters	$\alpha = \beta = 90^{\circ}, \ \gamma = 120^{\circ},$	$\alpha = \beta = 90^{\circ}, \ \gamma = 120^{\circ},$	$\alpha = \beta = 90^{\circ}, \ \gamma = 120^{\circ},$		
	$V = 80.41(90) \text{ Å}^3,$	$V = 79.95(2) \text{ Å}^3,$	$V = 77.30(6) \text{ Å}^3,$		
	Z = 4	Z = 4	Z = 4		
O (1/3, 2/3, z)	0.0792(3)	0.0746(5)	0.0692(3)		
Phase fractions	5.1(2)%	32.3(2)%	62.6(2)%		
Reliability factors		$R_{wp} = 7.59\%$			
	$R_p = 5.03\%$				
	<i>Gof</i> = 2.27				
		$R_F^2 = 5.49\%$			

Table S4. Crystallographic and Rietveld refinement data of the sample charged to 4.5 V.

Space group	P6 ₃ /mmc (194) - hexagonal		
Wavelengths	1.5406 Å		
Temperature	~300 K		
	a = b = 2.87831(19) Å,		
	<i>c</i> = 11.1629(11) Å		
Cell parameters	$\alpha = \beta = 90^{\circ}, \ \gamma = 120^{\circ}$		
	$V = 80.091(11) \text{ Å}^3,$		
	<i>Z</i> = 4		
Reliability factors	$R_{wp} = 7.43\%$		
	$R_p = 4.36\%$		
	<i>Gof</i> = 5.49		
	$R_F^2 = 8.05\%$		

Table S5. Crystallographic and Rietveld refinement data of the sample after 100 cycles.

	х	У	Z	Occupancy	$U_{ m iso}$	Wyckoff
Na1	0	0	1/4	0.503(1)	0.0632(7)	2 <i>d</i>
Na2	1/3	2/3	3/4	0.320(2)	0.0306(6)	2b
Mn	0	0	0	0.621(1)	0.0253(9)	2 <i>a</i>
Ni	0	0	0	0.282(1)	0.0253 (9)	2 <i>a</i>
Li	0	0	0	0.082(1)	0.0253 (9)	2 <i>a</i>
0	1/3	2/3	0.0641(6)	1.0	0.0901(3)	4 <i>f</i>

Table S6. Atomic coordinates, occupancies and isotropic displacement parameters ($Å^2$) after 100 cycles.

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