**Electronic Supplementary Information (ESI)** 

# P2-type $Na_{0.7}(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ cathode with excellent cyclability and rate capability for sodium ion batteries

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## Experimental

#### Sample preparation

Spherical  $(Ni_{0.6}Co_{0.2}Mn_{0.2})(OH)_2$  precursors were synthesized using co-precipitation method using NiSO<sub>4</sub>·6H<sub>2</sub>O, CoSO<sub>4</sub>·7H<sub>2</sub>O and MnSO<sub>4</sub>·H<sub>2</sub>O (Daejung Chemical Co.) as starting materials. A homogeneously mixed transition metal sulfates were slowly pumped into a continuously stirred tank reactor. Concurrently, 4 M NaOH (aq) and 2 M NH<sub>4</sub>OH chelating agent (aq) were also separately pumped into the reactor. After reaction, the precursor powders were obtained by filtering, washing, and vacuum drying at 110 °C for 12 h. For a typical synthesis of P2-type Na-MCM, the mixture of Na<sub>2</sub>CO<sub>3</sub> and  $(Ni_{0.6}Co_{0.2}Mn_{0.2})(OH)_2$  with a molar ratio of 0.7:1 was thoroughly ground, pressed into pellet, and annealed at 400 °C for 5 h and at 780 °C for 15 h in air followed by the quench process. The O3-type Na-NCM was prepared using Na<sub>2</sub>CO<sub>3</sub> and  $(Ni_{0.6}Co_{0.2}Mn_{0.2})(OH)_2$  with a molar ratio of 1.05:1. The mixture was annealed 650 °C for 15 h in air followed by furnace cooling process. Finally, the materials were immediately transferred to a glovebox under inert atmosphere.

## Materials Characterization

The chemical composition of the synthesized powders was determined using inductively coupled plasma atomic emission spectrometer (ICP-AES; OPTIMA 4300DV, Perkin-Elmer). The crystal structure was determined by synchrotron radiation powder X-ray diffraction (SPXRD) data collected at room temperature from the 9B HRPD beamline of the Pohang Accelerator Laboratory (PAL) and X-ray diffraction (XRD, D8 Advance, Bruker). The Rietveld refinement was performed by Fullprof program. The morphology was observed by scanning electron microscopy (SEM, SU-70, Hitachi). The Ni K-edge, Co K-edge and Mn K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were collected on the BL10C beam line at the Pohang Light Source (PLS-II) in Korea with top-up mode operation under a ring current of 200 mA at 3.0 GeV.

### *Electrochemical measurements*

The cathode was fabricated by blending the active materials (90 wt %), carbon black (Super P) (4 wt %), and polyvinylidene fluoride (PVDF) (6 wt %) in n-methyl-2-pyrrolidone (NMP). The resulting slurry was pasted onto aluminum foil and dried at 110 °C for 12 h in a vacuum oven. The electrochemical properties were evaluated using a CR2032 coin-type half cell. The electrolyte was 1.0 M NaClO<sub>4</sub> dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:2 v/v). The cells were galvanostatically charged and discharged between 2.0 and 4.0 V vs. Na<sup>+</sup>/Na at room temperature using a program controlled battery test system (WBCS 3000S WonATech). The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 1000 kHz to 1 mHz with an AC amplitude of 10 mV using a ZIVE SP1 potentiostat/galvanostat/EIS.



Fig. S1 SEM images of  $(Ni_{0.6}Co_{0.2}Mn_{0.2})(OH)_2$  precursor.

(a).						
()	Samples	Na		Ni	Co	Mn
-	(Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> )(OH) <sub>2</sub>	-		0.60	0.20	0.20
	O3-type Na(Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> )O <sub>2</sub>	0.97		0.60	0.20	0.20
-	P2-type Na <sub>0.7</sub> (Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> )O <sub>2</sub>	0.68	3	0.59	0.21	0.19
(b)_						
	Cathodes	a(Å)	c(Å)	Volume(Å)	Rwp(%)	Rp(%)
	O3-type Na(Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> )O <sub>2</sub>	2.9326	15.7918	117.64	8.45	6.58
	P2-type Na <sub>0.7</sub> (Ni <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> )O <sub>2</sub>	2.8542	11.2063	119.45	10.48	8.21

**Table S1** (a) ICP-AES results of hydroxide precursor and O3- and P2-type Na-NCMs and (b) lattice parameters of O3- and P2-type Na-NCMs determined by Rietveld refinement.



**Fig. S2** X-ray diffraction patterns of Na-NCMs synthesized at different annealing temperature, Na content, and cooling rate.



Fig. S3 Temeprature profiles of furnace cooling and air quenching.



**Fig. S4** X-ray diffraction pattern of as-syntheized P2-type Na-NCM after re-annealing at 780 °C and furmace-cooling.



Fig. S5 Cyclic voltammogram of (a) O3- and (b) P2-type Na-NCMs at a scan rate of 0.04 mV s<sup>-1</sup>.



Fig. S6 Voltage profile of P2-type Na-NCM electrode between 2.0-4.3 V (vs. Na/Na<sup>+</sup>).



**Fig. S7** Average working potential vs. gravimetric specific capacity for reported P2-type sodium layered cathode materials.

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**Fig. S8** *Ex-situ* XANES and EXAFS spectra of pristine, 1<sup>st</sup> charged, and 1<sup>st</sup> discharged P2-type Na-NCM electrode.



**Fig. S9.** Cycling performance of the P2-type Na-NCM electrode between 2.0 and 4.2 V (vs. Na/Na<sup>+</sup>) at the current density of 1 C.



**Fig. S10** (a, c) Nyquist plots and (b, d) relationships between real impedance and frequency for pristince and cycled O3- and P2-type Na-NCM electrodes, respectively.

Cycle	Cathodes	R <sub>sei</sub> (Ω)	R <sub>cτ</sub> (Ω)	D <sub>Na+</sub> (cm² S⁻¹)
Defense such	O3 type	-	235	2.24 x 10 <sup>-10</sup>
Before cycle	P2 type	-	270	3.52 x 10 <sup>-9</sup>
	O3 type	605	785	4.27 x 10 <sup>-12</sup>
Alter cycle	P2 type	-	372	2.45 x 10 <sup>-10</sup>

Table S2. Impedance parameters for O3- and P2-type Na-NCM electrodes.

The inclined line at low frequency in the Nyquist plots is related to the solid state diffusion of Na<sup>+</sup> ions in the layered structure. The Na<sup>+</sup> ion diffusion coefficient can be calculated based on the following equation [1,2]

$$R^2 T^2$$

$$D_{Na^+} = \frac{R^2 T^2}{2n^4 F^4 C^2 A^2 \sigma^2}$$

Where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of sodium ion, and  $\sigma$  is the Warburg factor which can be calulated according to the following equation.

$$Z_{\text{real}} = R_{\text{SEI}} + R_{\text{CT}} + \sigma \omega^{-1/2}$$

Where  $R_{SEI}$  is the resistance of the electrolyte and electrode material,  $R_{CT}$  is the charge transfer resistance, and  $\omega$  is the angular frequency in the low frequency region. The Na<sup>+</sup> diffusion coefficients of P2-type and O3-type Na-NCMs obtained in this study were within the reported range of Na<sub>x</sub>TMO<sub>2</sub> layered oxides [3].

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Fig. S11 Illustration of crystal structure for O3- and P2-type Na-NCMs.