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$_4$·6H$_2$O, CoSO$_4$·7H$_2$O and MnSO$_4$·H$_2$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$_4$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$_2$CO$_3$ 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$_2$CO$_3$ 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$_4$ 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$^+/Na$ 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 $(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})\text{(OH)}_2$ precursor.

![SEM images](image)

### 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.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Na</th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Ni}<em>{0.6}\text{Co}</em>{0.2}\text{Mn}_{0.2})\text{(OH)}_2$</td>
<td>-</td>
<td>0.60</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>O3-type Na$(\text{Ni}<em>{0.6}\text{Co}</em>{0.2}\text{Mn}_{0.2})\text{O}_2$</td>
<td>0.97</td>
<td>0.60</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>P2-type Na$<em>{0.8}$(Ni$</em>{0.6}$Co$<em>{0.2}$Mn$</em>{0.2}$)O$_2$</td>
<td>0.68</td>
<td>0.59</td>
<td>0.21</td>
<td>0.19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cathodes</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>Volume(Å$^3$)</th>
<th>Rwp(%)</th>
<th>Rp(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3-type Na$(\text{Ni}<em>{0.6}\text{Co}</em>{0.2}\text{Mn}_{0.2})\text{O}_2$</td>
<td>2.9326</td>
<td>15.7918</td>
<td>117.64</td>
<td>8.45</td>
<td>6.58</td>
</tr>
<tr>
<td>P2-type Na$<em>{0.8}$(Ni$</em>{0.6}$Co$<em>{0.2}$Mn$</em>{0.2}$)O$_2$</td>
<td>2.8542</td>
<td>11.2063</td>
<td>119.45</td>
<td>10.48</td>
<td>8.21</td>
</tr>
</tbody>
</table>
**Fig. S2** X-ray diffraction patterns of Na-NCMs synthesized at different annealing temperature, Na content, and cooling rate.

**Fig. S3** Temperature 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 furnace-cooling.

Fig. S5 Cyclic voltammogram of (a) O3- and (b) P2-type Na-NCMs at a scan rate of 0.04 mV s⁻¹.
Fig. S6 Voltage profile of P2-type Na-NCM electrode between 2.0-4.3 V (vs. Na/Na$^+$).
Fig. S7 Average working potential vs. gravimetric specific capacity for reported P2-type sodium layered cathode materials.


Fig. S8 *Ex-situ* XANES and EXAFS spectra of pristine, 1st charged, and 1st 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\(^+\)) 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.
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\textsuperscript{+} ions in the layered structure. The Na\textsuperscript{+} ion diffusion coefficient can be calculated based on the following equation \cite{1,2}

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

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 calculated according to the following equation.

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

Where \(R_{\text{SEI}}\) is the resistance of the electrolyte and electrode material, \(R_{\text{CT}}\) is the charge transfer resistance, and \(\omega\) is the angular frequency in the low frequency region. The Na\textsuperscript{+} diffusion coefficients of P2-type and O3-type Na-NCMs obtained in this study were within the reported range of Na\textsubscript{x}TMO\textsubscript{2} layered oxides \cite{3}.


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