# Supporting Information

# Integrating P2 into O´3 toward a Robust Mn-Based Layered Cathode for Sodium-Ion Batteries

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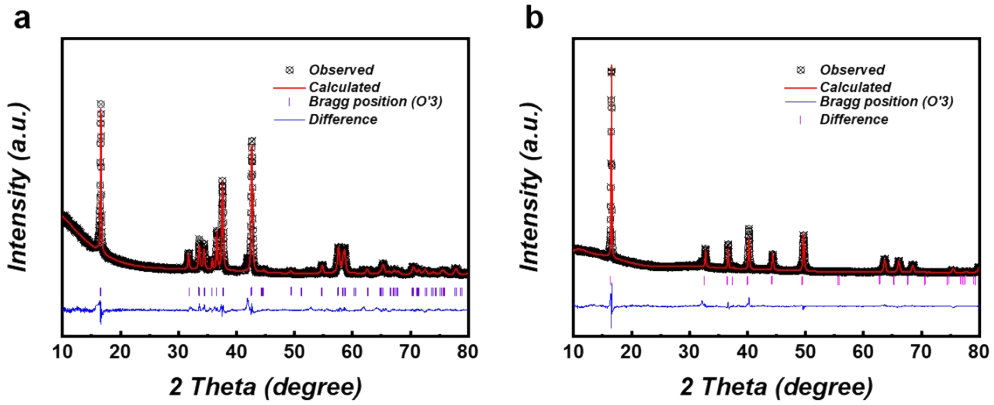


**Fig. S1** Rietveld refinement patterns of (a) O´3 $NaMnO_2$ (hereafter denoted as O´3 NMO) and (b) P2 $Na_{0.67}MnO_2$ (denoted as P2 NaMO) using lab X-ray Diffraction data.

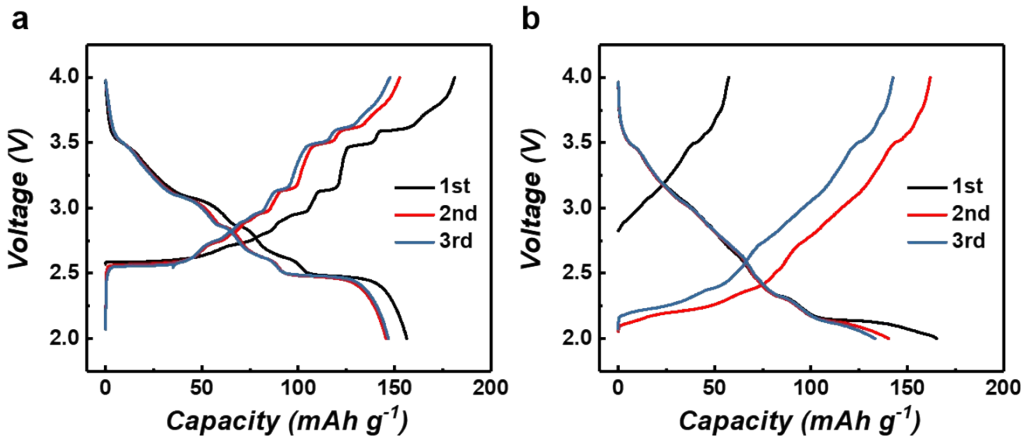


**Fig. S2** The galvanostatic charge/discharge curves at 0.1C in the voltage range of 2.0-4.0 V of (a) O´3 NMO and (b) P2 NaMO.

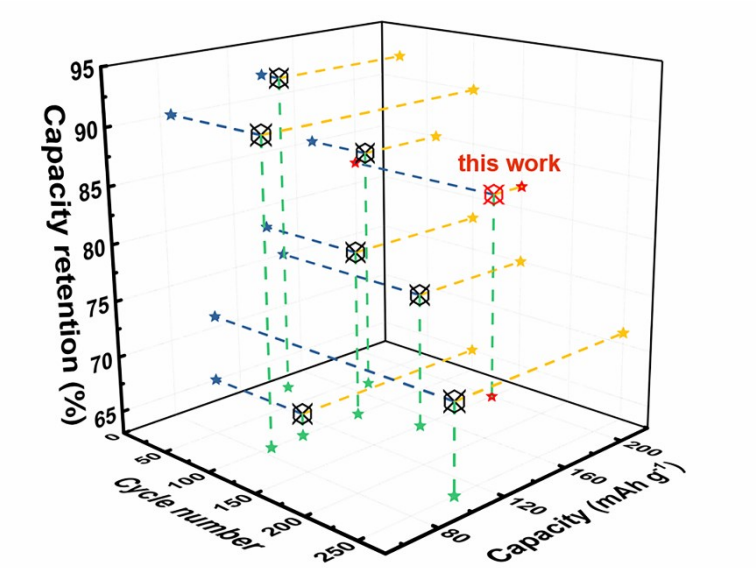


**Fig. S3** The Comparison of performance parameters including capacity, retention and cycle number between this work and other bi-phase structure materials.

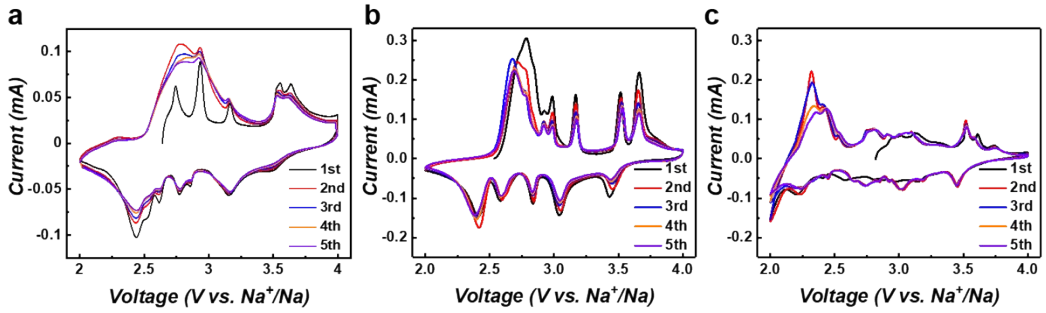


**Fig. S4** The Cyclic voltammogram of (a) P2/O´3 NMCSO, (b) O´3 NMO, and (c) P2 NaMO performed in the voltage region 2.0-4.0V at a scan rate of 0.1 mV $s^{-1}$.

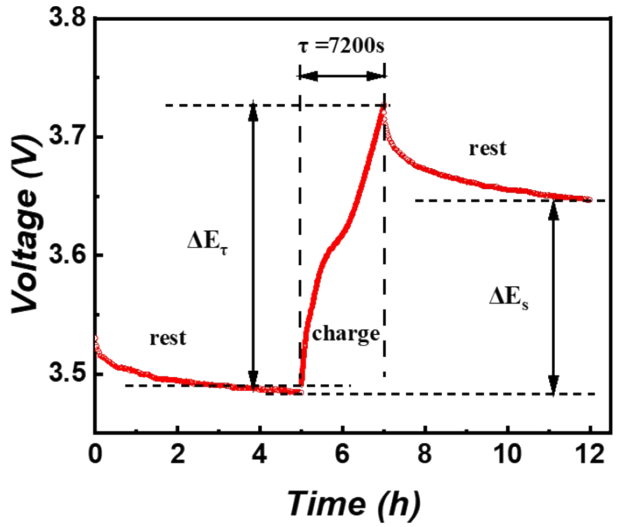


**Fig. S5** Detailed schematic diagram of a single-step GITT experiment at 0.1C in the voltage of ~3.5 V.

The GITT measurement was conducted to investigate the kinetics of sodium ions during the progresses of insertion and extraction. And the diffusion coefficients were determined according to the Equation S1.

$$D_{Na^+} = \frac{4}{\pi \cdot \tau}\left(\frac{m_B \cdot V_m}{M_B \cdot A}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad \left(\tau \ll L^2/D_{Na^+}\right) \qquad \text{Equation S1}$$

D is the diffusion coefficient, $\tau$ is the pulse duration (7200s), $m_B$ is the mass of the active materials, $V_m$ is the molar volume, $M_B$ is the molecular mass, A is the surface area, $\Delta E_s$ and $\Delta E_\tau$ are obtained via GITT curves as shown in Fig S5.

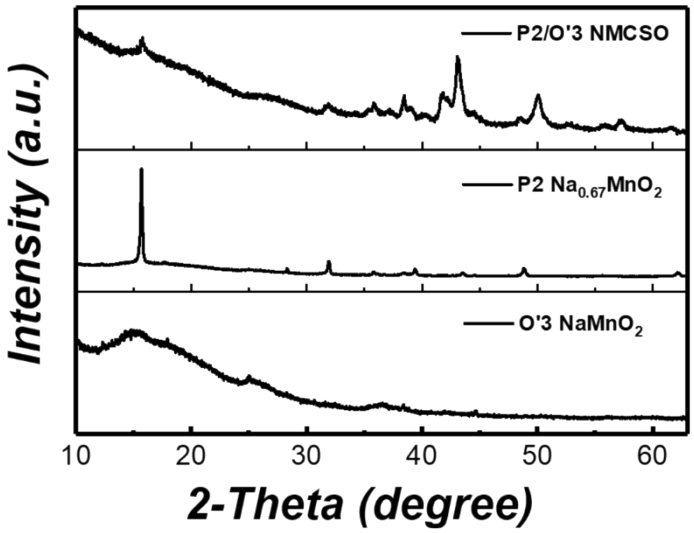


**Fig. S6** The XRD patterns of cathode electrodes that experience 200 charging and discharging cycles.

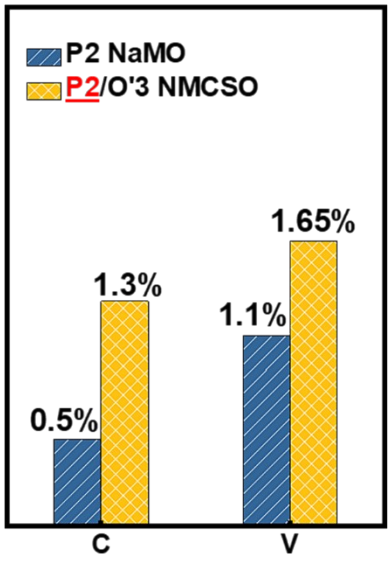


**Fig. S7** The comparison of parameters c and volume between P2/O´3 NMCSO and the P2 compound.

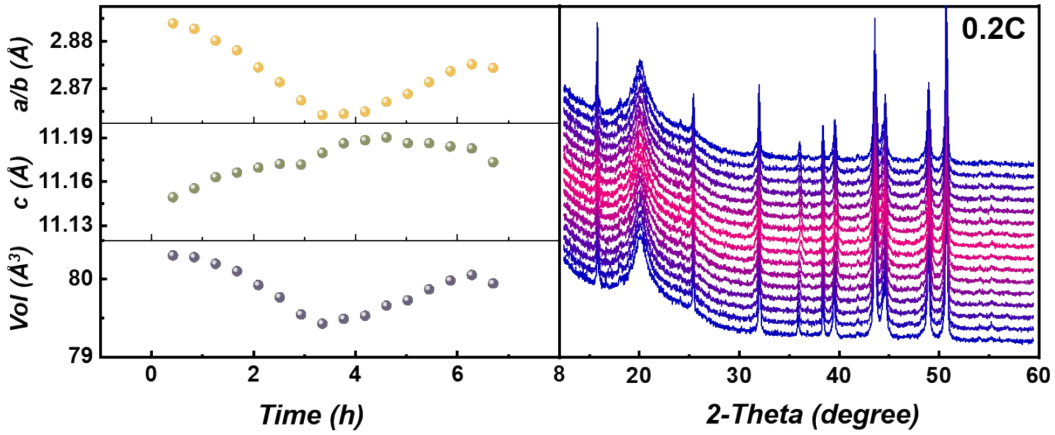


**Fig. S8** Structure transformation of P2 NaMO electrode utilizing in situ XRD and evolution of lattice parameters a, b, c and volume during the electrochemical sodiation/desodiation process.

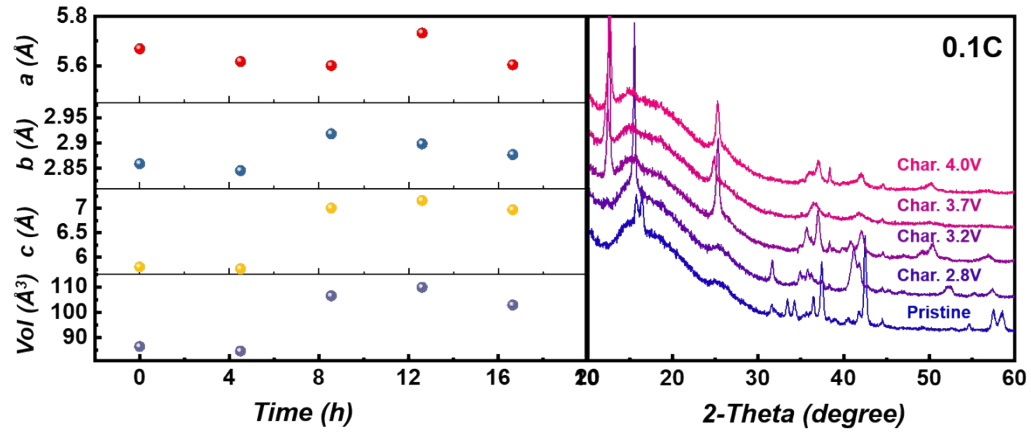


**Fig. S9** Structure transformation of O´3 NMO electrode utilizing ex situ XRD and evolution of lattice parameters a, b, c and volume during the electrochemical sodiation/desodiation process.

**Table S1.** The results of ICP-AES experience.

| Theoretical chemical formula | Measured atomic ratio | | | |
|---|---|---|---|---|
| | Na | Mn | Cu | Sb |
| $NaMn_{0.9}Cu_{0.067}Sb_{0.033}O_2$ | 1.005 | 0.890 | 0.080 | 0.029 |

**Table S2.** Lattice parameters of the P2/O´3 NMCSO compound sample after Rietveld refinement.

| Phase | | P2 | O´3 |
|---|---|---|---|
| Space Group | | P63/mmc | C2/m |
| Cell Parameters | a(Å) | 2.89482 | 5.65073 |
| | b(Å) | 2.89482 | 2.86438 |
| | c(Å) | 11.17161 | 5.80847 |
| | α(°) | 90.000 | 90.000 |
| | β(°) | 90.000 | 112.948 |
| | γ(°) | 120.000 | 90.000 |
| | volume(Å$^3$) | 81.075 | 86.574 |
| Agreement Factors | $R_{wp}$(%) | 6.75 | |
| | $R_p$(%) | 4.63 | |
| | $\chi^2$ | 4.24 | |
| | Phase Ratio | 46.144 | 53.856 |

**Table S3.** Lattice parameters of the P2 $Na_{0.67}MnO_2$ and O´3 $NaMnO_2$ compound samples after Rietveld refinement.

| Phase | | P2 $Na_{0.67}MnO_2$ | O´3 $NaMnO_2$ |
|---|---|---|---|
| Space Group | | P63/mmc | C2/m |
| Cell Parameters | a(Å) | 2.87777 | 5.66622 |
| | b(Å) | 2.87777 | 2.85731 |
| | c(Å) | 11.1446 | 5.80144 |
| | α(°) | 90.000 | 90.000 |
| | β(°) | 90.000 | 113.144 |
| | γ(°) | 120.000 | 90.000 |
| | volume(Å$^3$) | 79.929 | 86.367 |
| Agreement Factors | $R_{wp}$(%) | 8.67 | 10.16 |
| | $R_p$(%) | 6.33 | 6.42 |
| | $\chi^2$ | 4.74 | 4.47 |

**Table S4.** The results of EIS experiments fitted via the following equivalent circuit.

| Sample | $R_s$(Ω) | $R_1$(Ω) | $R_{ct}$(Ω) |
|---|---|---|---|
| P2/O´3 NMCSO | 3.341 | 60.3 | 57.2 |
| O´3 NMO | 9.704 | 60.89 | 482.9 |