Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

New Electrode Material for Rechargeable Sodium Batteries: P2-type $Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ with Anomalously High Reversible Capacity

Naoaki Yabuuchi,[1,2] Ryo Hara,[1] Kei Kubota,[1] Jens Paulsen[3], Shinichi Kumakura[4], and Shinichi Komaba[1,2*]

[1]Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo, 162-8061, Japan

[2]Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto, 615-8520, Japan

[3]Umicore Korea Limited, 401, Chaam-dong, Cheonan-city, Chungnam, 330-200, Korea

[4]Umicore Japan KK, Kobe Plant, 4-2-8 Minami-machi, Minatojima, Chuo-ku, Kobe, 650-0047, Japan

*E-mail: komaba@rs.kagu.tus.ac.jp

Electrochemical characterization of P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ in Na cells;

Composite positive electrodes consisted of 80 wt% active materials, 10 wt% acetylene black and 10 wt% poly(vinylidene fluoride), pasted on aluminum foil as a current collector. The electrodes were dried at 80 °C in vacuum. Metallic sodium (Kanto Chemical) was used as a negative electrode. The electrolyte solution used was 1.0 mol dm^{-3} $NaClO_4$ dissolved in the mixture of propylene carbonate and dimethyl carbonate (50 : 50 by volume, Kishida Chemical) with fluorinated ethylene carbonate (2 vol.%) as an electrolyte additive. A microporous polyolefin membrane was used as a separator. R2032-type coin cells were assembled in the Ar-filled glove box. Sample loading of active materials was specified in the caption of **Figure 2**. The coin cells were cycled in the voltage range of 1.5 and 4.4 V at a rate of 10 mA g^{-1}.

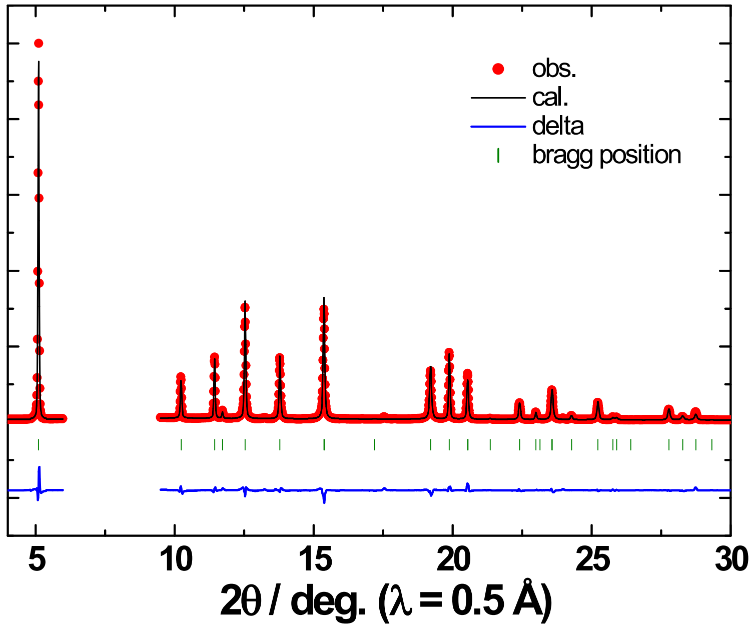

Figure S1. The result of the Rietveld analysis on the SXRD pattern of P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$. Refined crystallographic parameters are summarized in Table 1. Rietveld analysis was conducted except the region, of 2 theta = 6.0 – 9.5 degrees, corresponding to the 3.0 – 4.8 Å of *d*-values because through-plane staking faults of the superlattice layers are observed.

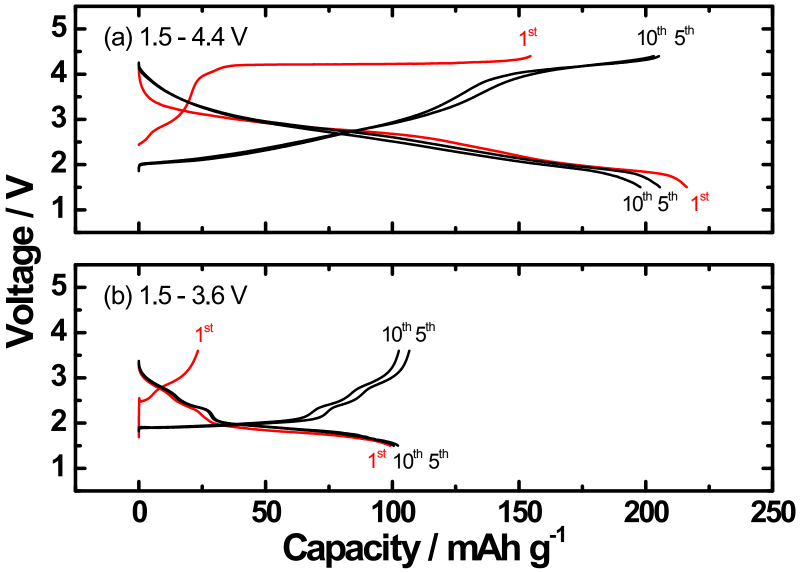

Figure S2. Galvanostatic charge and discharge curves of Na/$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ cells with different cut-off voltage; (a) 4.4 and (b) 3.6 V. Reversible capacity is significantly increased by charge to high voltage of 4.4 V.

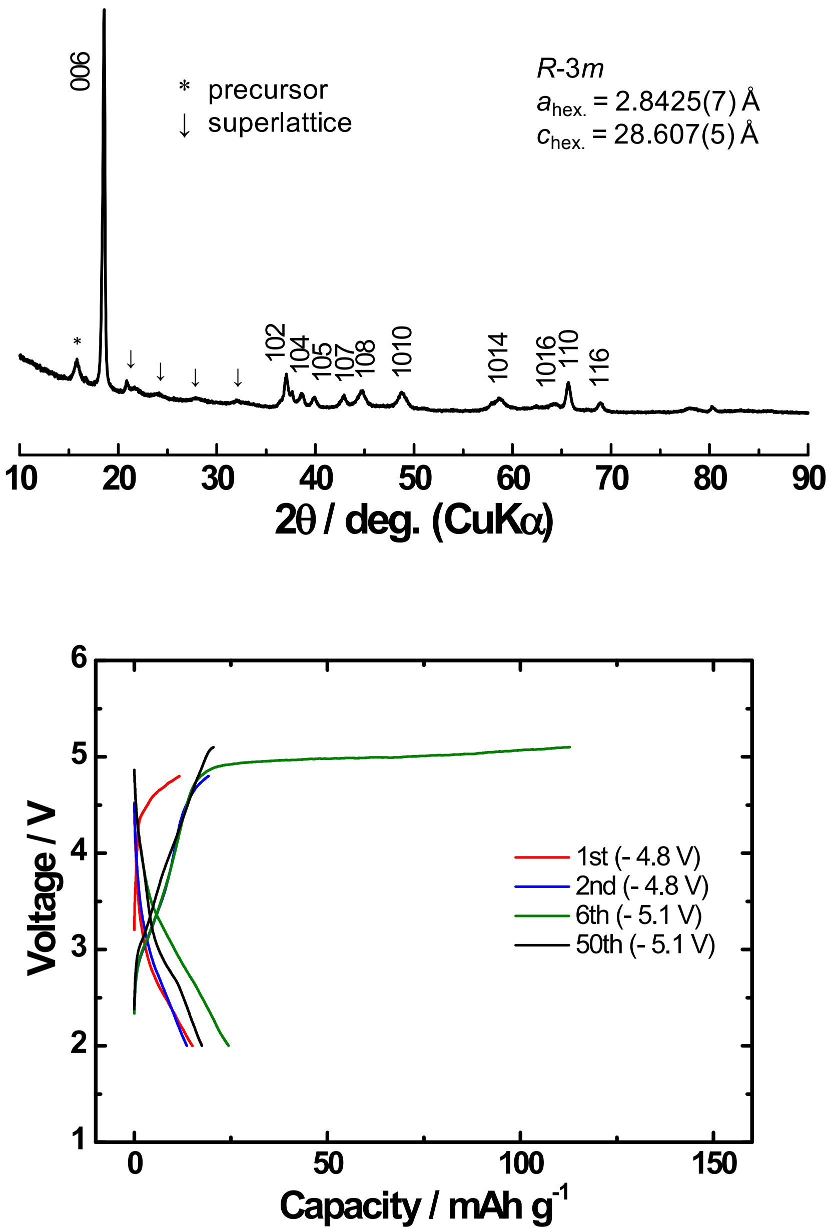

Figure S3. Na^+/Li^+ ion-exchange of P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ in a molten salt and its electrode performance in a Li cell: (top) A XRD pattern of Na^+/Li^+ ion-exchanged P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ in a molten salt of $LiNO_3$: LiCl (= 88 : 12 in mol%) at 350 °C for 6 h, according to the method described in the literature (J. M. Paulsen, C. L. Thomas, and J. R. Dahn, *J. Electrochem. Soc.,* 1999, **146**, 3560.). This phase is assigned into O6-type layered phase with small amount of the precursor. The formation of O6-type phase is the consistent result with the literature (Reference 12). The formation of O6-phase by heat-treatment at 350 °C has been also reported in $Li_{2/3}Co_{1/3}Mn_{2/3}O_2$ (S. Komaba, L. Croguennec, F. Tournadre, P. Willmann, and C. Delmas, *J.*

Phys. Chem. C, 2013, **117**, 3264.), which is highly active as electrode materials. (bottom) Electrode performance of the ion-exchanged sample in a Li cell: Voltage plateaus have not been observed in the Li cell by charge to 4.8 V vs. Li. Although a voltage plateau is observed on charge to 5.1 V, large discharge capacity, as observed in Na cells, is not obtained. This plateau could originate from the electrolyte decomposition.

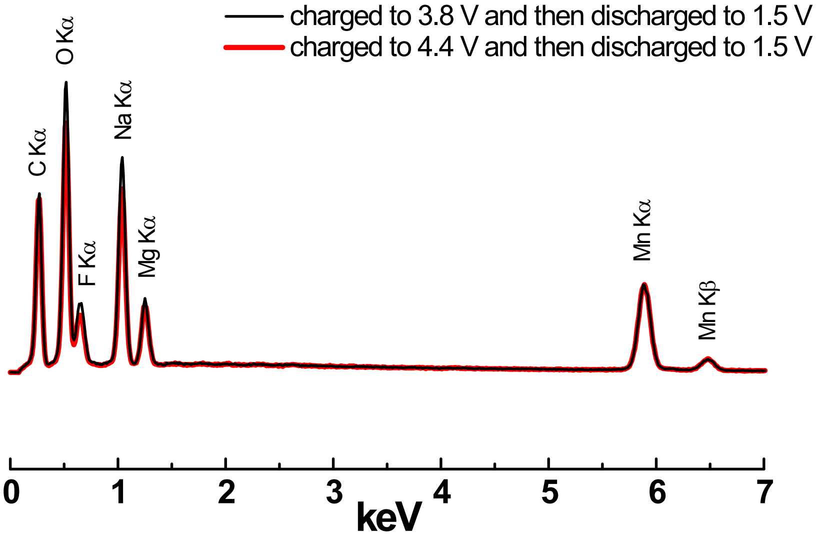

Figure S4. Chemical analysis by energy-dispersive X-ray spectroscopy (EDX). P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ electrodes are charged to 3.6 and 4.4 V and then discharged to 1.5 V in Na cells. From the EDX spectra, it is unlikely to extract magnesium ions from $Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ even by charge to 4.4 V.

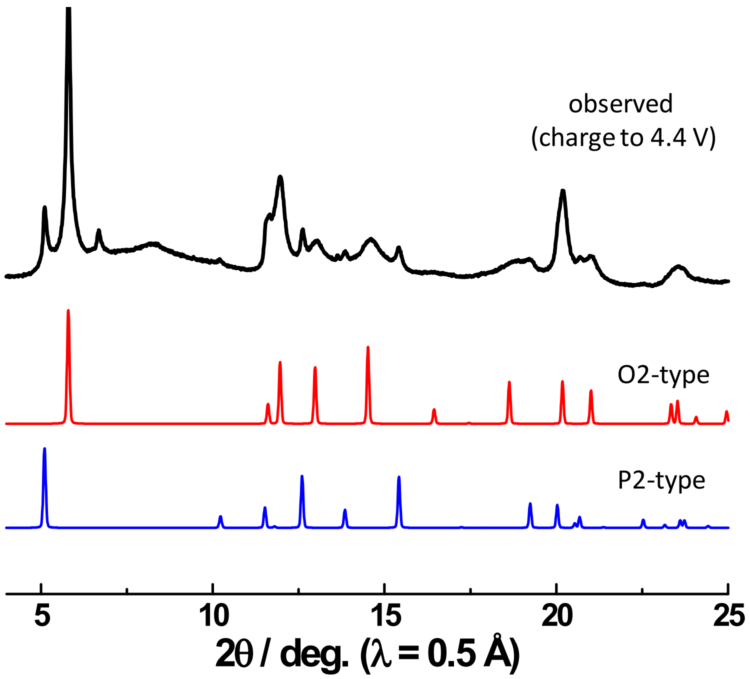

Figure S5. The SXRD pattern of the $Na_x[Mg_{0.28}Mn_{0.72}]O_2$ electrode after full charge to 4.4 V. Simulated XRD patterns of O2- and P2-phases are also shown in the bottom.

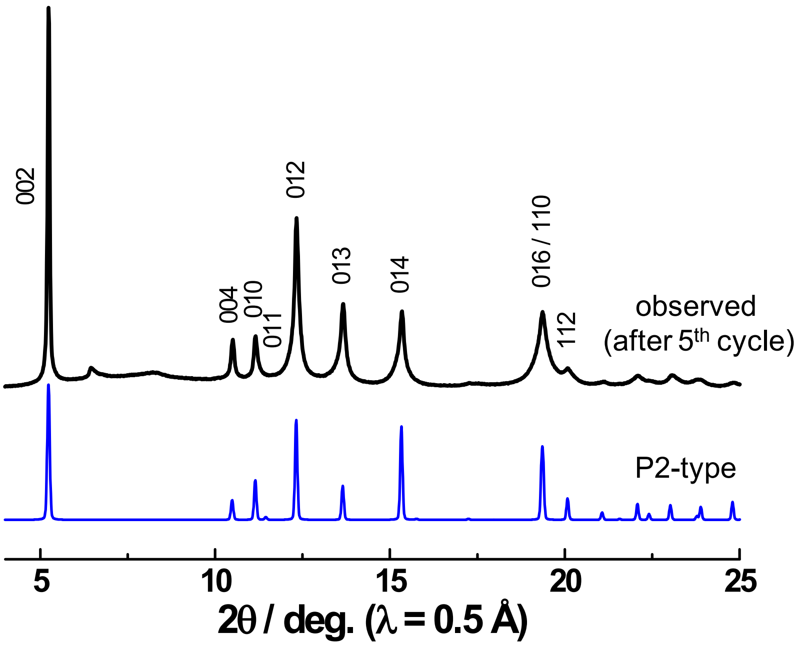

Figure S6. The SXRD pattern of the $Na_x[Mg_{0.28}Mn_{0.72}]O_2$ electrode after 5 cycles in the Na cell. A simulated XRD pattern of the P2-phase is also shown in the bottom.

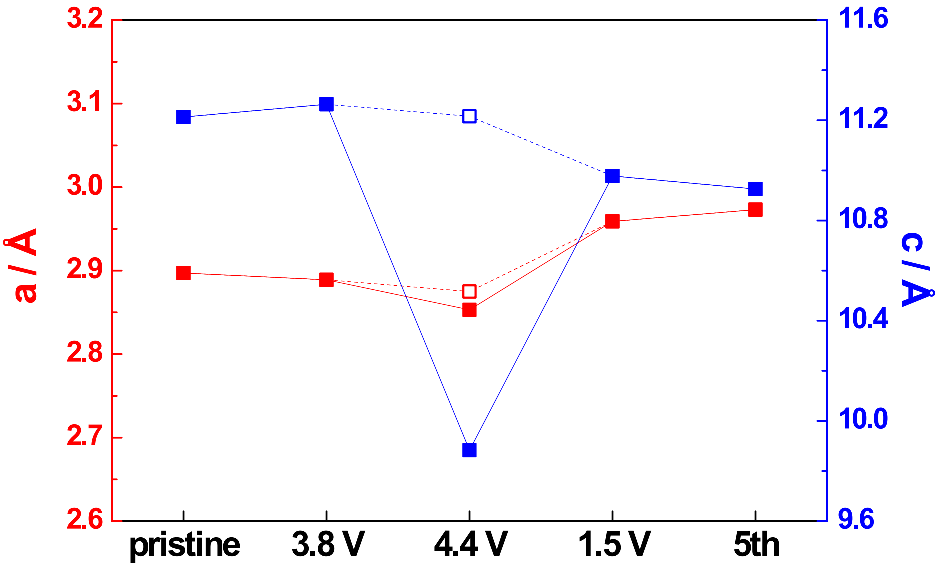

Figure S7. Changes in lattice parameters calculated from the SXRD patterns of $Na_x[Mg_{0.28}Mn_{0.72}]O_2$ in **Figure 3**. For the sample charged to 4.4 V, two phases, O2 phase (major phase) and P2 phase (minor phase), are found. Lattice parameters of the P2 minor phase are plotted as open symbols.