

## Supporting Information for

### Nanosize Cation-Disordered Rocksalt Oxides; Na<sub>2</sub>TiO<sub>3</sub>-NaMnO<sub>2</sub> Binary System

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## Supporting Experimental

Target materials were synthesized following a binary system of  $x \text{ Na}_2\text{TiO}_3 - (1 - x) \text{ NaMnO}_2$  by mechanical milling. Two end-members,  $\text{Na}_2\text{TiO}_3$  and  $\text{NaMnO}_2$ , were first prepared by solid-state calcination.  $\text{Na}_2\text{TiO}_3$  was prepared at 850 °C in air from  $\text{Na}_2\text{CO}_3$  (99.5%; Wako Pure Chemical Industries) and anatase  $\text{TiO}_2$  (98.5%, Wako Pure Chemical Industries) as starting materials.  $\text{NaMnO}_2$  was obtained by calcination of a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  at 800 °C in Ar.  $\text{Mn}_2\text{O}_3$  was obtained by heating  $\text{MnCO}_3$  (Kishida Chemical) at 850 °C for 12 h in air. Mixtures of  $\text{NaMnO}_2$  and  $\text{Na}_2\text{TiO}_3$  were mechanical milled using a planetary ball mill (Pulverisette 7, Fritsch) and a zirconia pot (45 mL) and zirconia balls (15.5 g). After milling for 12 h at 600 rpm, the mixtures were retrieved from the container and mixed using a mortar and pestle. The mixtures were again milled using the zirconia pot and balls at 600 rpm for 12 h. This process was repeated four or three times. Overall, the total milling time was 48 h for the sample of  $x = 0.34$  and 36 h for the samples of  $x = 0.22$  and 0.5. To further increase the electric conductivity as electrode materials, thus obtained powders were ball milled with acetylene black (HS-100; Denka) at 300 rpm for 6 h.

Crystal structures of the samples were examined by using an X-ray diffractometer equipped with a high-speed position sensitive detector (D2 PHASER, Bruker). Synchrotron X-ray diffraction (XRD) data were collected at beamline BL02B2 at SPring-8 in Japan. The

measurement was conducted using an automatic powder diffraction system equipped with the MYTHEN detector in Debye-Scherrer geometry with powder samples in glass capillaries.[1] The wavelength was calibrated to be 0.5003 Å with CeO<sub>2</sub> diffraction data used as a standard reference sample.

The morphological features of the samples were observed using a scanning electron microscope (JEOL, JCM-6000) and transmission electron microscope (JEOL, JEM-ARM200F). Hard X-ray absorption spectroscopy (XAS) at Mn K-edge was performed at beamline BL-9C of Photon Factory in Japan. Hard XAS spectra were collected with a silicon monochromator in a transmission mode. Soft XAS spectra (O K-edge and Mn L<sub>II, III</sub>-edges) were collected at BL-11 of SR Center in Ritsumeikan University. Soft XAS spectra were collected with fluorescence yield and electron yield modes. Normalization of the XAS spectra was carried out using the Athena software.[2]

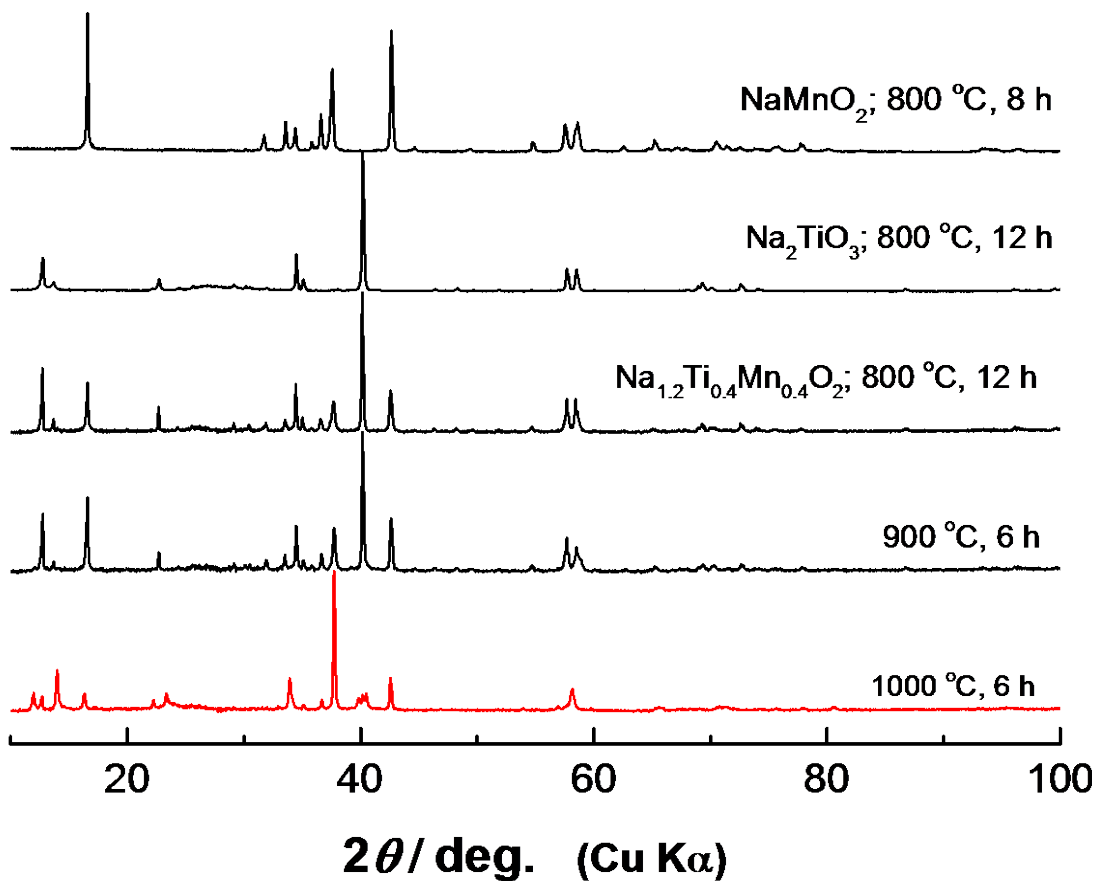
Electrode performance of the samples was examined in Na cells. The composite positive electrodes consisted of 76.5 wt% as-prepared sample, 13.5 wt% acetylene black and 10 wt% poly(vinylidene fluoride), pasted on aluminum foil as a current collector. The composite electrodes were dried at 120 °C in vacuum. Metallic sodium was used as a negative electrode. Electrolyte solution used was 1.0 mol dm<sup>-3</sup> NaPF<sub>6</sub> dissolved in propylene carbonate (battery grade; Kishida Chemical). A glass filter was used as separator (GB-100R, Advantec). Two-

electrode cells (TJ-AC, Tomcell Japan) were assembled in the Ar-filled glove box and cycled at a rate of 10 mA g<sup>-1</sup> at room temperature. The samples for *ex-situ* measurements were prepared by taking out the composite electrodes from the cells after washing with propylene carbonate and dimethyl carbonate in the glove box.

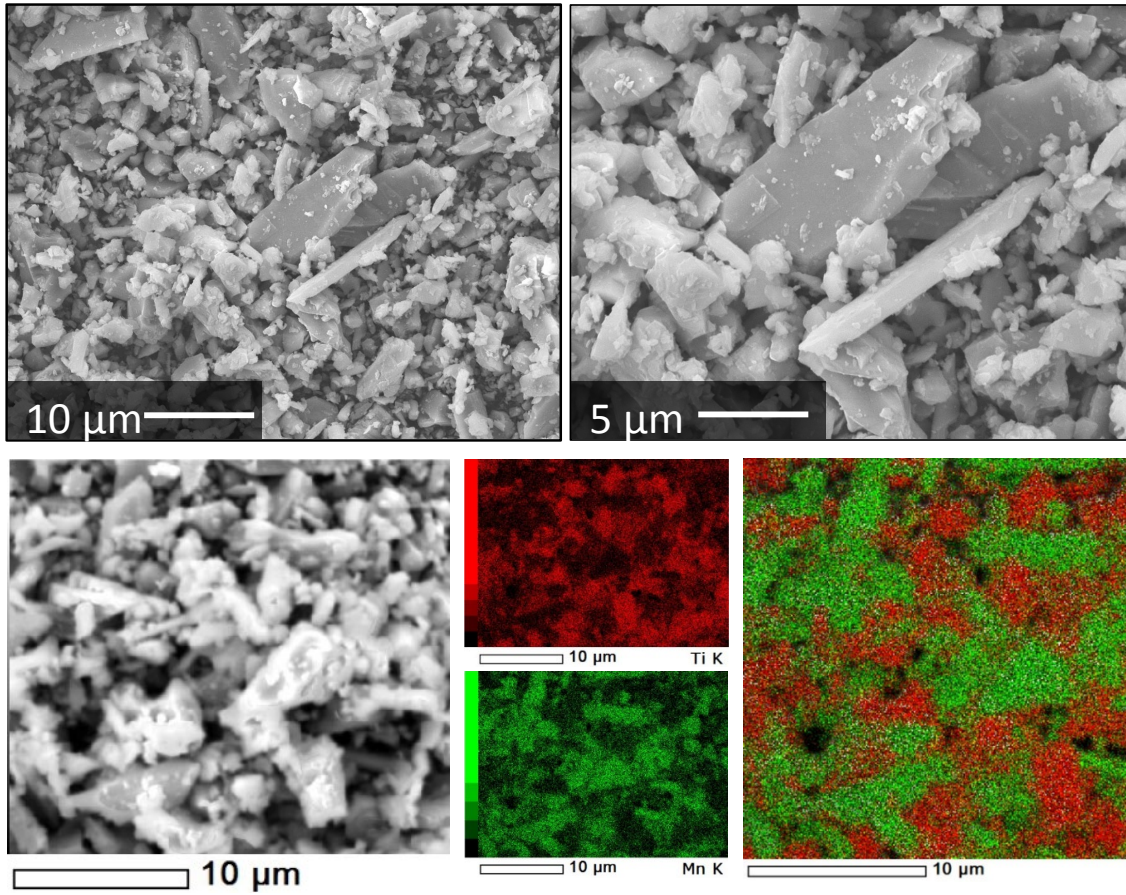
### Supporting References

1. Kawaguchi, S.; Takemoto, M.; Osaka, K.; Nishibori, E.; Moriyoshi, C.; Kubota, Y.; Kuroiwa, Y.; Sugimoto, K., *Review of Scientific Instruments* **2017**, *88*. DOI 10.1063/1.4999454.
2. Newville, M., *J. Synchrot. Radiat.* **2001**, *8*, 322-324.

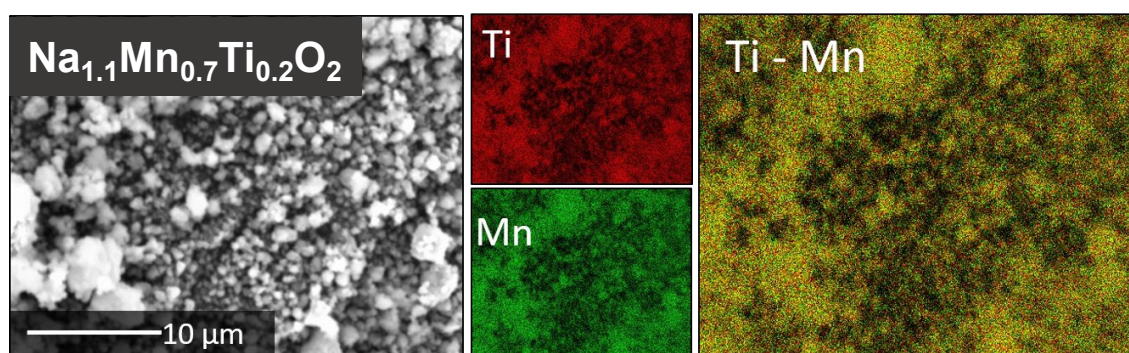
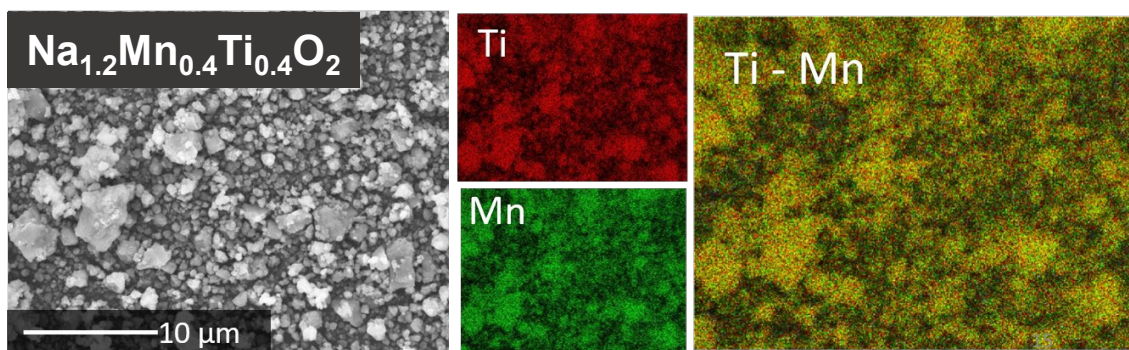
Supporting Figures



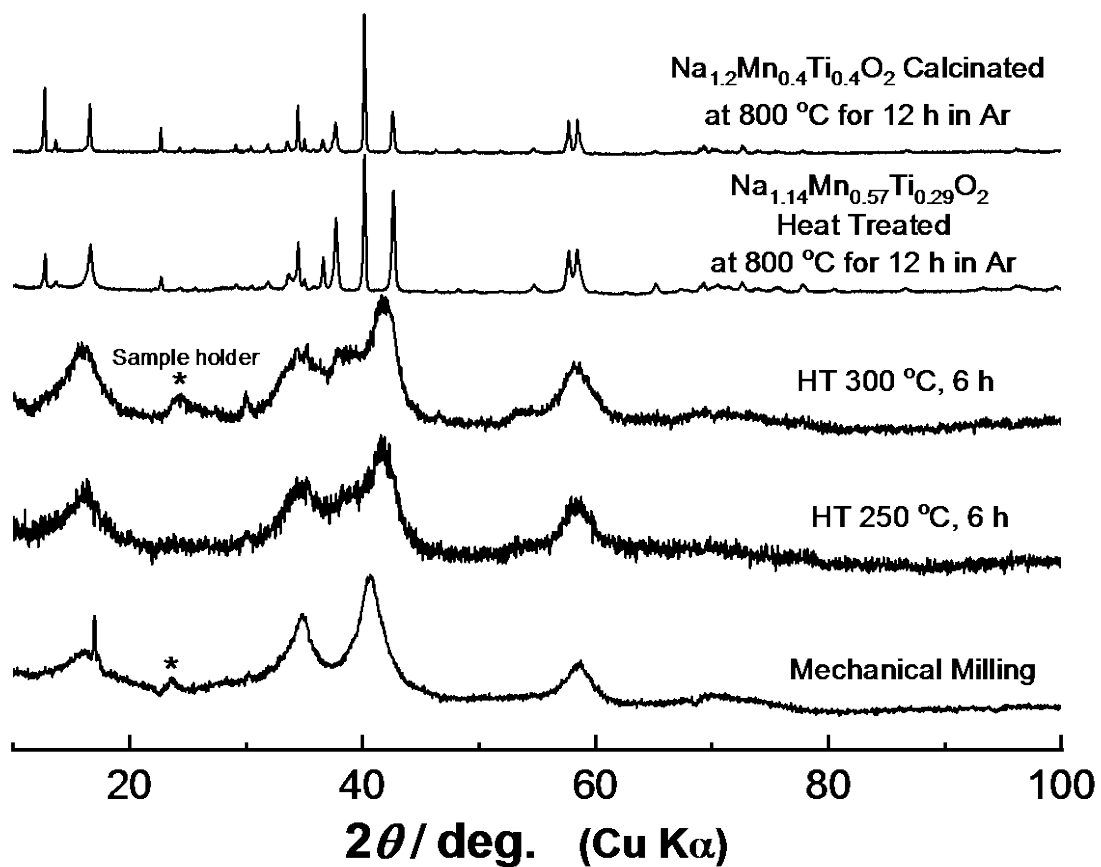
**Figure S1.** XRD patterns of the sample with a nominal composition of  $\text{Na}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$  prepared by solid-state calcination method. A single phase sample cannot be obtained by these experimental conditions.



**Figure S2.** SEM images and EDX elemental maps of the sample with a nominal composition of  $\text{Na}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$  prepared by solid-state calcination method at 1000 °C. Phase segregation is clearly evidenced from the EDX maps.

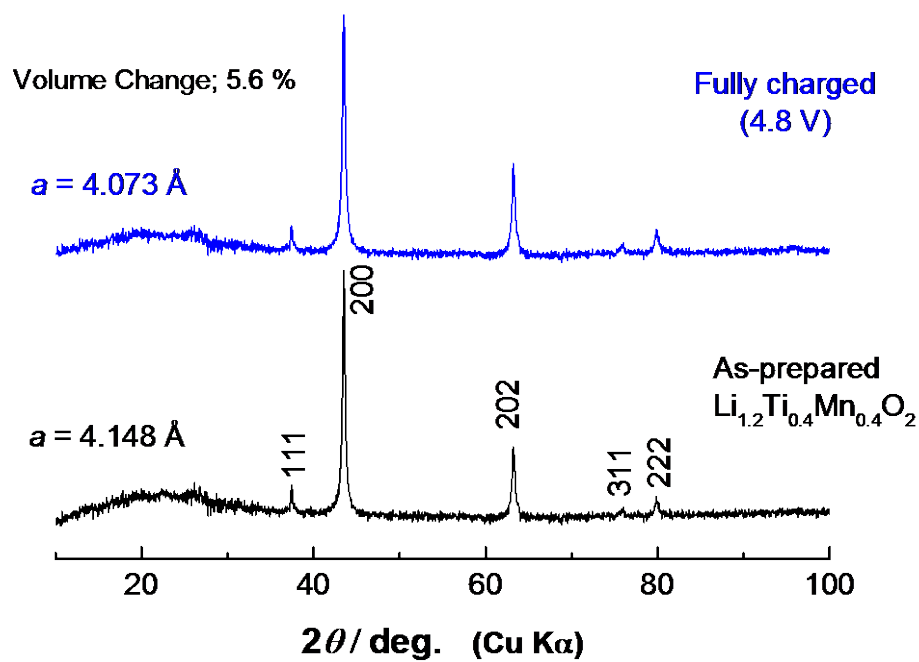


**Figure S3.** SEM images and EDX elemental maps of  $\text{Na}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$  and  $\text{Na}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$  synthesized by mechanical milling.

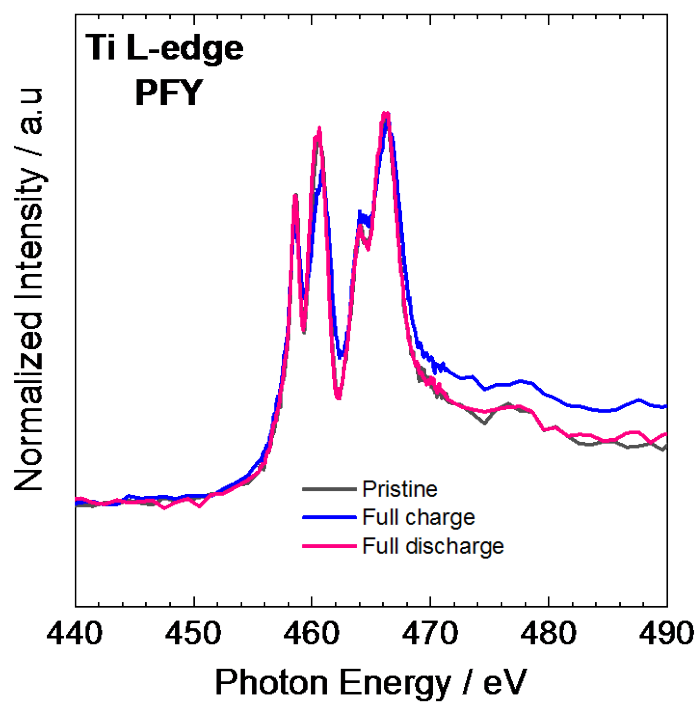


**Figure S4.** XRD patterns of  $\text{Na}_{1.14}\text{Mn}_{0.57}\text{Ti}_{0.29}\text{O}_2$  prepared by mechanical milling after heating at different temperatures.





**Figure S5.** *Ex-situ* XRD patterns of  $\text{Li}_{1.2-y}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$  before and after charge to 4.8 V.



**Figure S6.** Ti L-edge XAS spectra of  $\text{Na}_{1.14-y}\text{Mn}_{0.57}\text{Ti}_{0.29}\text{O}_2$  on the initial charge/discharge process.