

Supplemental Information of
Study of the interface between Na-rich and Li-rich
phases in a Na-inserted spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystal for an
electrode of a sodium-ion battery

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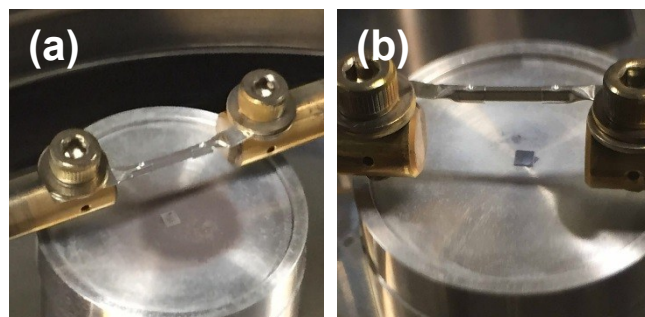


Figure S1

(a) Photograph of a LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) crystal specimen just after the Na evaporation.

A square-shaped small thin specimen is located at the center of an Al stand within a dark stain caused by deposited Na metal. (b) Photograph of the same specimen after being kept in a high-vacuum condition (5×10^{-5} Pa) for 28h. The color of the square-shaped specimen turned black, indicating that the reduction reaction of Ti^{4+} proceeded, which means the Na-insertion reaction occurred in the LTO specimen.

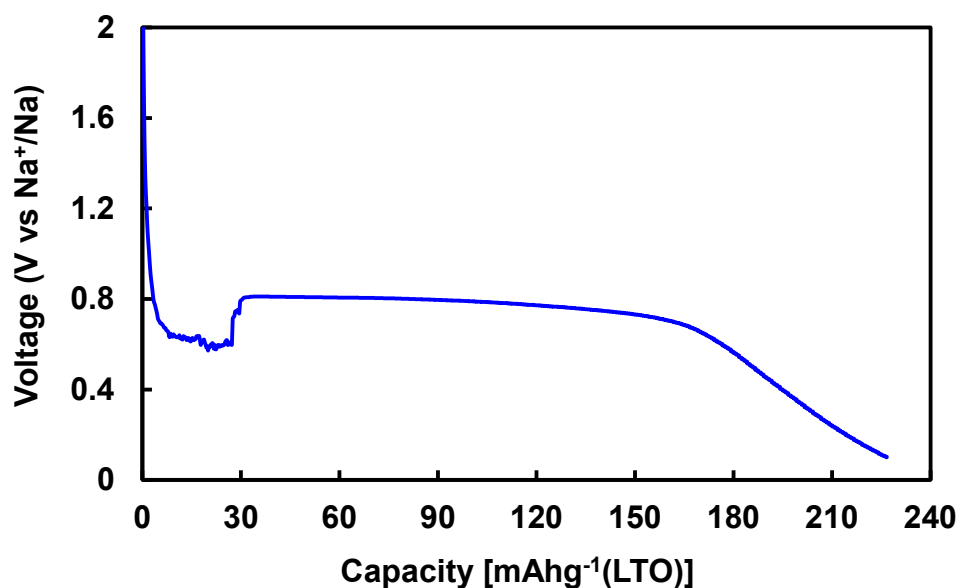


Figure S2

Cell-voltage profile of the electrochemical Na insertion during the in-situ XRD measurement of the LTO electrode. The experiment was performed under a constant current density of 3 mA g^{-1} from OCV (around 2V) to 0.1 V vs Na^+/Na . The capacity was about 200 mAhg^{-1} for 0.3 V as the cut-off condition. However, this should contain extra capacity by side reactions of carbon additives, which was estimated as about 20 mAhg^{-1} for the present electrode configuration.²³ Thus the net capacity is almost the same as the theoretical capacity of the net LTO content in the electrode, indicating that almost all the LTO particles are involved in the Na insertion. The over voltage drop observed at the initial Na-insertion stage (till 30 mAhg^{-1}) may contain some artifact of electrochemical measurement.

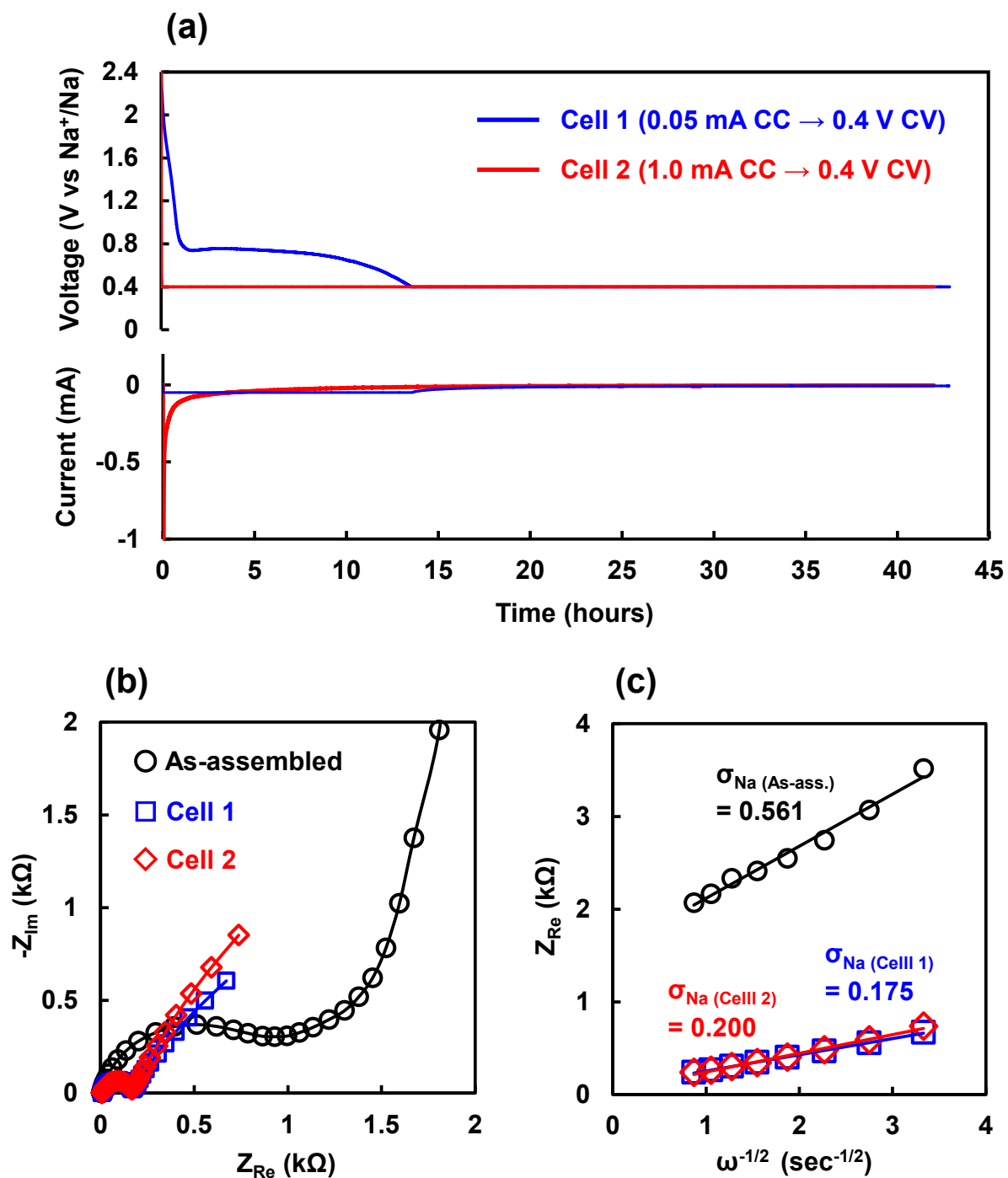


Figure S3

Investigation of Na-ion behavior at LTO-electrode/electrolyte interfaces and inside pristine and Na-inserted LTO electrodes by electrochemical impedance spectroscopy (EIS).

For Na-inserted LTO electrodes, we prepared two sample cells (cells 1 and 2) by different Na-insertion rates. Cells 1 and 2 were discharged till 0.4 V (vs Na⁺/Na) with the constant current of 0.05 mA and 1.0 mA (about 10 mA_g⁻¹ and 200 mA_g⁻¹ of current densities), respectively. Then both the cells were kept at 0.4 V till 43 h under the constant voltage condition. The electrochemical profiles of these cells are shown in (a), where blue and red lines show the time variation of the voltage and current values of cells 1 and 2. Required time of voltage decay into 0.4 V was 15 h and 2 min for cells 1 and 2, respectively. The Na-insertion rate for the electrode of cell 2 is much faster than that of cell 1. After 43 h, the circuit current of both the cells reached almost 0 mA, indicating the completion of Na insertion with relaxed microstructures. The total quantity of electric charge was about 1.0 and 0.9 mAh for cells 1 and 2, respectively, indicating 180 and 160 mA_h⁻¹ of reaction quantity of the LTO electrode, which are almost equal to the theoretical capacity. Thus the Na insertion was completely performed in each LTO electrode.

To investigate the electrode property of these Na-inserted cells as well as the cell of a pristine LTO electrode, EIS measurement was performed with the frequency range of 10 kHz -10 mHz at AC amplitude of 5 mV in the open circuit condition. The Nyquist plots of the cells are shown in (b). The charge transfer resistance at the electrode/electrolyte interface, measured by the diameter of semi-circle, is 1.0 kΩ for the pristine cell and 0.2 kΩ for both the Na-inserted cells. The lower resistance of the Na-inserted cells can be explained by the presence of Na-LTO phases on the surfaces of electrode particles, while some surface layers such as solid-electrolyte interphases may be involved. No remarkable differences between cells 1 and 2 suggest that different Na-insertion rates do not induce significant differences for the surface properties of electrode particles.

In order to obtain Na-ion diffusion coefficients in electrode particles, we plotted typical $Z_{(Re)}-\omega^{-1/2}$ relation in each cell in (c). The slope of linear plots provides the magnitude

of Warburg factor σ ,²³ which has typical relation with the Na-ion diffusion coefficient D as follows.²³

$$\sigma \propto \frac{1}{\sqrt{D}}$$

The diffusion coefficients for the Na-inserted cells were evaluated as $D_{(\text{Cell 1})} = 10.3 D_{(\text{As-ass.})}$ and $D_{(\text{Cell 2})} = 7.9 D_{(\text{As-ass.})}$. It is apparent that Na-ion diffusion is much faster in the Na-inserted electrodes than that in the surface regions of pristine LTO-crystal particles, due to the presence of Na-LTO phases with large lattice expansion. On the other hand, the coefficients of both the Na-inserted cells were not so different from each other, suggesting that the properties of Na-LTO phases are not so affected by the Na-insertion rate. Of course, the microstructures in Na-inserted LTO particles may possibly depend on the Na-insertion rate in spite of similar EIS results, which should be investigated in the future.

References

23 M. Kitta, K. Kuratani, M. Tabuchi, R. Kataoka, T. Kiyobayashi, M. Kohyama, *Electrochemistry*, 2015, **83**, 989-992.