Discovery of the Na-substituted spinel phase generation in the Li$_4$Ti$_5$O$_{12}$ electrode during high-voltage discharge reaction of Na-ion battery cycling.

*Mitsunori Kitta and Masanori Kohyama
Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST) 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, JAPAN

Address for correspondence: E-mail: m-kitta@aist.go.jp

Spinel-type lithium titanium oxide (LTO, Li$_4$Ti$_5$O$_{12}$) is one of the promising materials for a negative electrode of a sodium-ion battery,[1,2] However, the Na-insertion reaction of LTO (a = 8.36 Å) usually generates (Na$_{6b}$)$_{16c}$Li$_{Ti5}$$_{16d}$(O$_{12}$)$_{32e}$ (a = 8.72 Å)[3], which involves an extremely large volume increase. It is desirable to prepare a Na-substituted spinel phase, (Na$_{3b}$)$_{8a}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$, because its Na-insertion form, (Na$_{6b}$)$_{16c}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$, is considered to show a small lattice-volume change. This material was not yet confirmed so far. Here we discovered that the Na-substituted spinel phase can be really formed in a discharged LTO electrode of a Na-ion battery.

Fig. 1(a) shows voltage profiles of two kinds of discharge experiments of fully Na-inserted LTO electrode, consisting of (Na$_{6b}$)$_{16c}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$ and (Li$_{6b}$)$_{16c}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$. In one process, the discharge voltage is kept under the Li-extraction potential (1.2 V vs Na*/Na) at 1.1 V, as shown by a grey solid line. In the other process, it is over the Li-extraction potential as shown by a black solid line. Fig. 1(b) shows their corresponding XRD profiles. The electrode discharged under the Li-extraction voltage only shows clear peaks assigned as LTO (▼) with a = 8.36 Å, indicating that only the Na ions were extracted from the fully Na-inserted LTO electrode, leading to the natural recovery of LTO. On the other hand, for the electrode discharged over the Li-extraction voltage, we can see extra peaks marked with black arrows, assigned as a spinel phase of a = 8.69 Å with high intensity of 220 reflection, indicating the generation of (Na$_{3b}$)$_{8a}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$ in addition to usual LTO. This is because both Na and Li ions were extracted equally with a discharge voltage over the Li-extraction potential, resulting in the formation of Na-remaining oxidized phase in the electrode particle as (Na$_{3b}$)$_{8a}$(Li$_{Ti5}$)$_{16d}$(O$_{12}$)$_{32e}$.

![Fig. 1 Phase alternation of LTO electrode with various discharge voltage profiles. (a) Typical two types of discharge profiles of fully Na-inserted LTO electrode with constant voltage control under (grey) and upper (black) the Li-extraction voltage. (b) X-ray diffraction spectra of corresponding experiment for (a).](image)

References: