Discovery of the Na-substituted spinel phase generation in the $Li_4Ti_5O_{12}$ electrode during high-voltage discharge reaction of Na-ion battery cycling.

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Spinel-type lithium titanium oxide (LTO, $Li_4Ti_5O_{12}$) 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 $(Na_6)^{16c}(LiTi_5)^{16d}(O_{12})^{32e}$ (a = 8.72 Å)[3], which involves an extremely large volume increase. It is desirable to prepare a Na-substituted spinel phase, $(Na_3)^{8a}(LiTi_5)^{16d}(O_{12})^{32e}$, because its Na-insertion form, $(Na_6)^{16c}(LiTi_5)^{16d}(O_{12})^{32e}$, 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 $(Na_6)^{16c}(LiTi_5)^{16d}(O_{12})^{32e}$ and $(Li_6)^{16c}(LiTi_5)^{16d}(O_{12})^{32e}$. 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 $(Na_3)^{8a}(LiTi_5)^{16d}(O_{12})^{32e}$ 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 $(Na_3)^{8a}(LiTi_5)^{16d}(O_{12})^{32e}$.

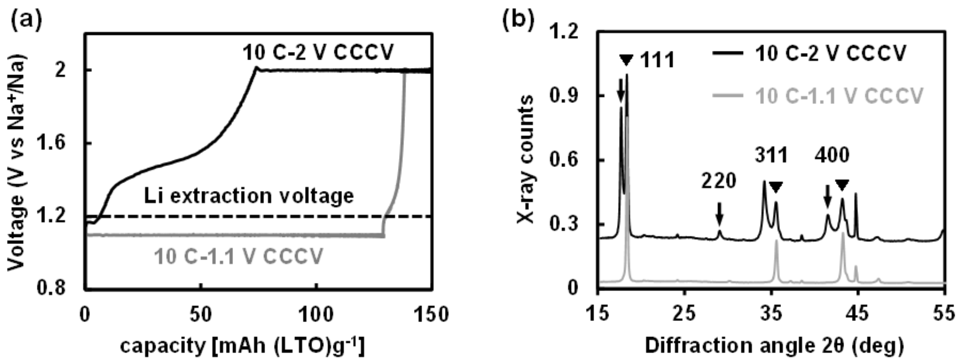

Fig. 1 Phase alternation of LTO electrode with various discharge voltage profiles. (a) Typical two types of discharge profiles of fully Na-inserted LTO electrode with constant voltage control under (grey) and upper (black) the Li-extraction voltage. (b) X-ray diffraction spectra of corresponding experiment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

References:

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[2] M. Kitta, K. Kuratani et. al., Electrochim. Acta 148 (2014) 175-179.

[3] Y. Sun, L. Zhao et. al., Nat. Commun. 4 (2013) 1870.