**Supplemental Information for Readers**

**S1. Discharge-charge curves of Nb:SrTiO3 substrate**

Fig/Fig_rev160531/Fig.S1_1a.pdf

Fig/Fig_rev160531/Fig.S1_1b.pdf

**Figure S1.** Discharge-charge curves of Nb-doped SrTiO3(111) substrates with (a) a NR cell and (b) a coin-type cell using an electrolyte of 1moldm-3 LiPF6 PC.

Fig/Fig_rev160531/Fig.S2_1.pdf

**Figure S2.** O 1s and Ti 2p XPS spectra of epitaxial Li4Ti5O12(111) film in pristine condition. The XPS data were collected with a spectrometer (Axis ultra, Ktatos) using focused monochromatized Al Ka radiation (1486.6eV). The pass energy was 20eV with a resolution of 0.37(2)eV, and the energy step was 0.1eV. The pressure in the chamber during analysis was under 10-7 Torr and the XPS spectra were analyzed using CasaXPS software. The Ti 2p3/2 peak of Ti4+ in the Li4Ti5O12 lattice was used as a reference peak position (458.7eV) for the energy calibration of XPS spectra.