

## Supporting Information

### **On the capacity degradation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ during long-term cycling in terms of composition and structure**

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#### 1) Preparation of Pure LTO

All reagents involved in this work are analytically pure and were used as received. The preparation of pure LTO is as follows, 2.6 g  $\text{LiOH}\cdot\text{H}_2\text{O}$  was dissolved in deionized water, then 28.2 g tetrabutyl titanate (TBT) dissolved in absolute ethyl alcohol was slowly titrated into the  $\text{LiOH}$  solution under magnetic stirring for 30 min. The mixture was dried thoroughly at 105 °C followed by sintering at 750 °C for 5 h in air atmosphere to achieve the pure LTO.

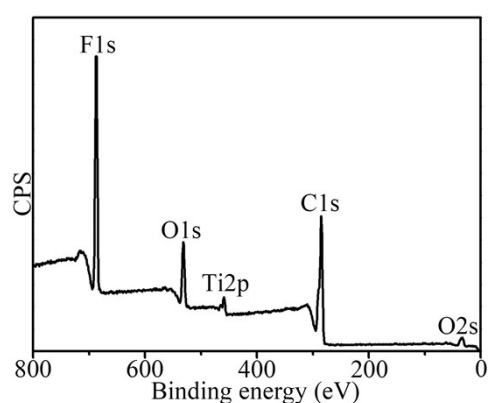
#### 2) Electrochemical Measurement

The electrochemical performance of LTO was evaluated by assembling 2025 coin-type half cells. The slurry containing pure LTO, acetylene black and polyvinylidene fluoride (PVDF) (with a mass ratio of 8: 1: 1) mixed in N-Methyl Pyrrolidone was uniformly coated on copper foil and thoroughly dried at 120 °C for 12 h in a vacuum oven. The cell assembly was performed in a glove box full of argon utilizing lithium foil as counter electrode, celgard 2300 as separator, 1 M LiPF<sub>6</sub> (dissolved in ethylene carbonate and dimethyl carbonate with the volume ratio of 1: 1) as electrolyte. Galvanostatic discharge/charge was adopted on a Land CT2001A battery test system at 25 °C with a voltage range of 1-2.5 V and a current density of 500 mA g<sup>-1</sup>. Cyclic voltammograms (CV) were tested on an Iviumstat electrochemistry workstation at a scanning rate of 0.3 mV s<sup>-1</sup> between 1 and 2.5 V vs Li/Li<sup>+</sup>. Electrochemical impedance spectra (EIS) were measured with an AC signal amplitude of 5 mV in the frequency range from 100 kHz to 0.01 Hz.

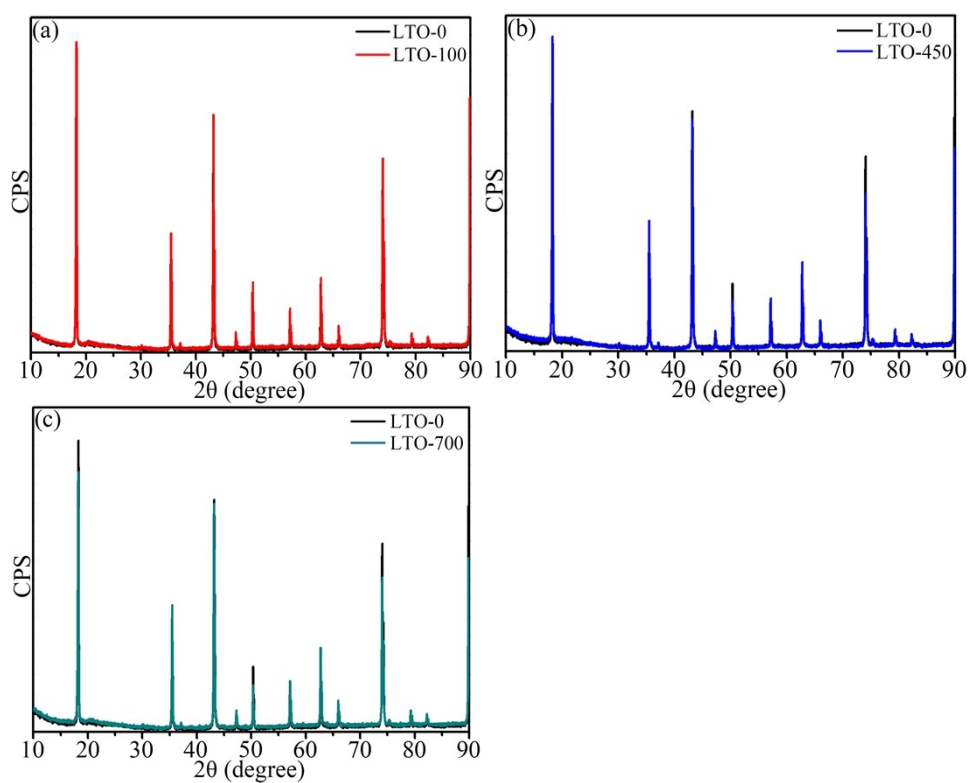
### 3) Materials Characterization

The coin-cells cycled at 500 mA g<sup>-1</sup> for various cycles were characterized by several techniques to understand the structure and composition changes in the LTO anode, and the active material was collected from the electrodes undergoing various cycle times. A Rigaku Dmax-2500 diffractometer with Ni filtered Cu K $\alpha$  radiation (V = 40 kV, I = 40 mA) was used to detect X-ray diffraction (XRD) patterns at a scanning rate of 10° min<sup>-1</sup>. A Lab-RAM HR800 Raman spectroscopy with 632.81 nm laser excitation was employed to acquire Raman spectra. A JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) was adopted for morphology

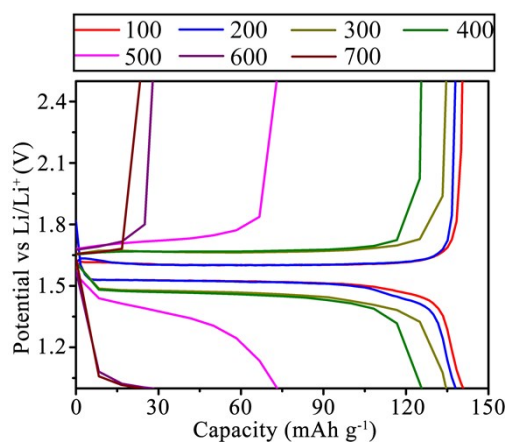
and microstructure examination. X-ray photoelectron spectra (XPS) were analyzed on a KARTOS XSAM800 X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, U.K.) using Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) as the excitation source ( $V = 12$  kV,  $I = 10$  mA).



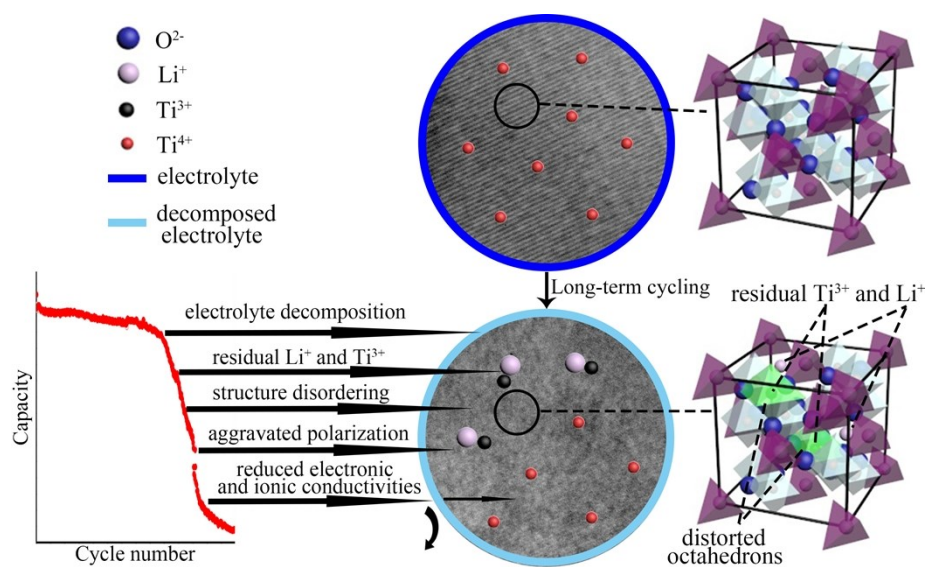
**Fig. S1** XPS survey spectrum for pure LTO.



**Fig. S2** XRD patterns of LTO-0 and LTO-100 (a), LTO-0 and LTO-450 (b) and LTO-0 and LTO-700 (c) for revealing structure disordering with cycling.



**Fig. S3** Discharge/charge plots for LTO after different cycles.



**Fig. S4** Schematic illustration for the factors leading to the performance degradation of LTO during long-term cycling at  $0.5 \text{ A g}^{-1}$ .