

Electronic Supplementary Information

One-step fabrication of a $\text{Li}_{3.33}\text{Cu}_{1.005}\text{Ti}_{4.665}\text{O}_{12}/\text{CuO}$ composite for lithium-ion batteries: a high-performance spinel with $P4_332$ space group and synergistic effect of substituting and compositing

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Experimental

Cu^{2+} -modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were synthesized by one-step solid-state reaction from Li_2CO_3 (Merck, 99.99%), TiO_2 (Sigma–Aldrich, 99.9%) and CuO (Aldrich, 99.99%). The chemicals were mixed at a predetermined molar ratio of Li: Cu: Ti = 1.07 : 0.5 : 1.5, ball-milled for 4 h by a Spex ball-milling machine (SPEX 8000M), and calcined at 800 °C for 4 h in air atmosphere. For comparison purposes, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3.4}\text{Cu}_{0.9}\text{Ti}_{4.7}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CuO}$ were also synthesized. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.4}\text{Cu}_{0.9}\text{Ti}_{4.7}\text{O}_{12}$ were prepared by the same process except that the ratios of Li: Cu: Ti are respectively 4.28 : 0 : 5 and 3.64: 0.9 : 4.7. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CuO}$ was fabricated through simple grinding the mixture of the resultant $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (91.69 wt%) and CuO (8.31 wt%) in a mortar.

Crystal structures of the as-calcined powders were identified by X-ray diffractions combined with Rietveld refinements. Step-scan diffraction profiles were recorded from an X-ray diffractometer (Shimadzu XRD-7000) between 10° and 125° with a step of 0.03° and a counting time of 8 s per step. Rietveld refinements were performed using the GSAS program with the EXPGUI interface [S1,S2]. Morphologies and particle sizes of the powders were examined using a field emission scanning electron microscopy (FESEM, Hitachi-4300).

Spinel/Li 2016 coin cells were fabricated in a recirculating argon glove box. The working electrodes contain 80 wt% active materials, 10 wt% super P conductive carbon (TIMCAL Ltd.) and 10 wt% polyvinylidene fluoride (PVDF, Aldrich) on copper foils. Lithium foils were employed as counter and reference electrodes, and microporous polypropylene membranes (Celgard 2400) were used as separators. Electrolyte is a mixed solvent of ethylene carbonate, dimethyl carbonate and diethylene carbonate (1:1:1 by weight) containing of 1 M LiPF_6 (DAN VEC). The loading density of the active materials in the cells was $\sim 2.0 \text{ mg cm}^{-2}$. Galvanostatic discharge/charge tests were conducted using a multi-channel battery testing system (LANHE CT2001A) within a potential range of 3–0.02 V. Cyclic voltammetry (CV) measurements were carried out using a Solartron Analytical 1470E CellTest System.

The detailed process of Rietveld refinements

In the two refinements, the site occupancies were assumed to fulfill the stoichiometric compositions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{4-2x}\text{Cu}_{3x}\text{Ti}_{5-x}\text{O}_{12}/\text{CuO}$, respectively. All isotropic temperature factors were fixed to be the same. The distributions of ions were fixed as follows. For $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with $Fd\bar{3}m$ space group, O^{2-} ions were distributed at the 32e sites, Li^+ and Ti^{4+} ions filled 8a sites, and Li^+ and Ti^{4+} ions stayed at 16d sites; and for $\text{Li}_{4-2x}\text{Cu}_{3x}\text{Ti}_{5-x}\text{O}_{12}$ with $P4_332$ space group, O^{2-} ions were placed at 8c and 24e sites, Li^+ and Cu^{2+} ions resided at 8c sites, Li^+ , Ti^{4+} and Cu^{2+} ions shared 4b sites, and Ti^{4+} ions occupied 12d sites. The total occupancies for all the sites were fixed to unity. During the refinements, a few instrumental and structural parameters were varied and refined, including background parameters, zero-shift, unit cell parameters,

profile parameters, atomic fractional coordinates, atomic isotropic displacement parameters and atomic occupancies. The ion distributions shown in Fig. 2a and Fig. 2b are those give the best fits.

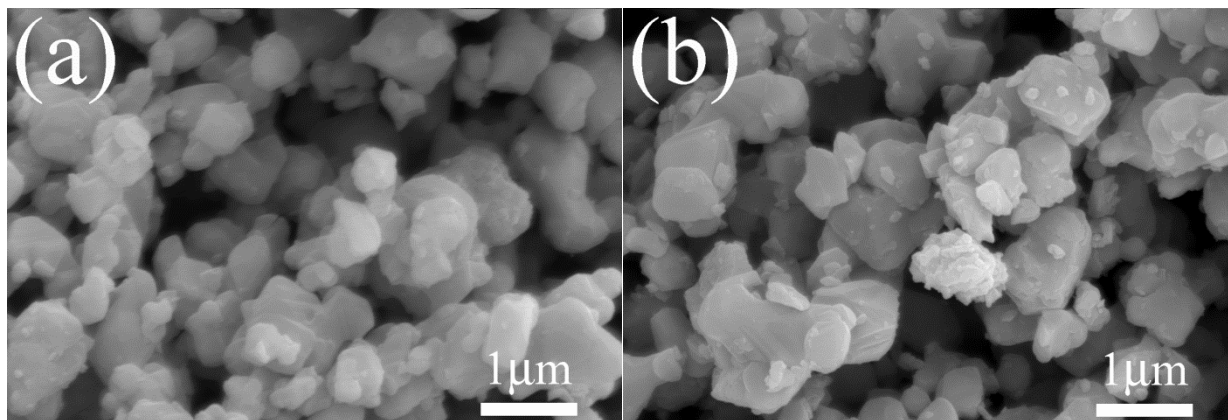


Fig. S1. FESEM images of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) $\text{Li}_{3.33}\text{Cu}_{1.005}\text{Ti}_{4.665}\text{O}_{12}/\text{CuO}$.

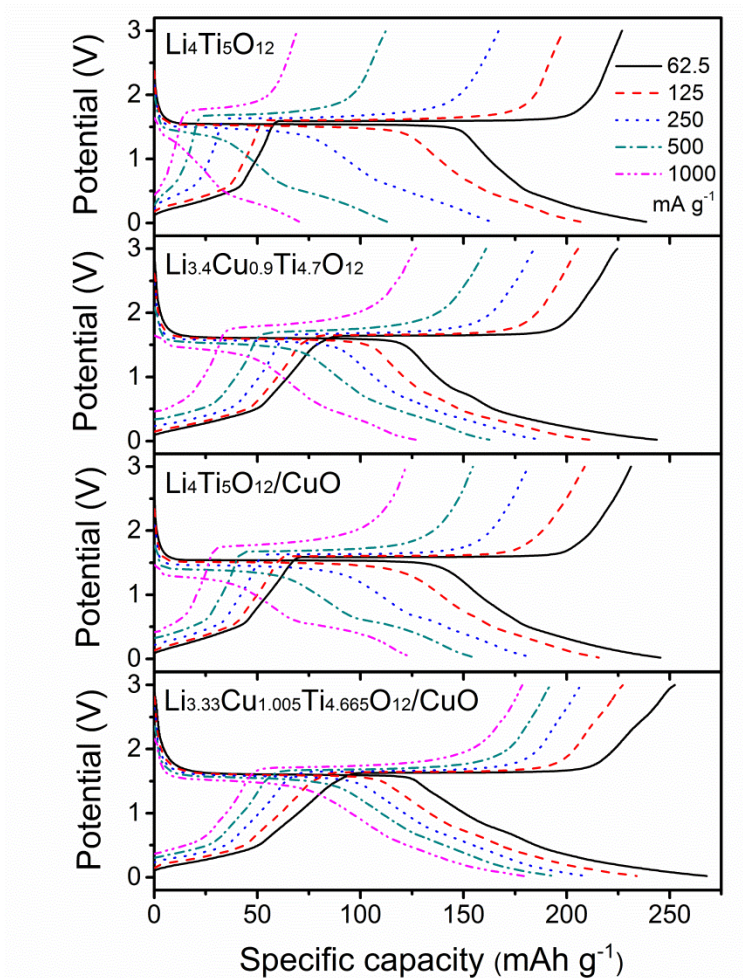


Fig. S2. Second discharge–charge profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3.4}\text{Cu}_{0.9}\text{Ti}_{4.7}\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CuO}$ and $\text{Li}_{3.33}\text{Cu}_{1.005}\text{Ti}_{4.665}\text{O}_{12}/\text{CuO}$ at $62.5\text{--}1000\text{ mA g}^{-1}$. Identical discharge–charge rates were used.

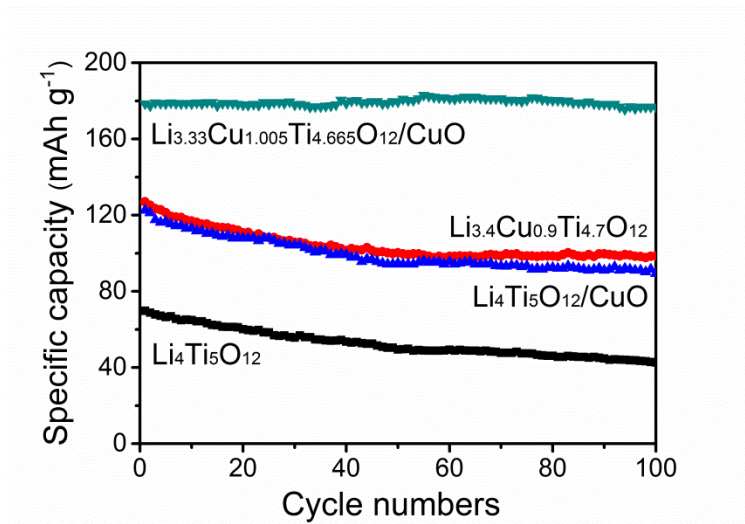


Fig. S3. Cyclic stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3.4}\text{Cu}_{0.9}\text{Ti}_{4.7}\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CuO}$ and $\text{Li}_{3.33}\text{Cu}_{1.005}\text{Ti}_{4.665}\text{O}_{12}/\text{CuO}$ at 1000 mA g^{-1} . Identical discharge–charge rates were used.

As shown in Fig. S2 and Fig. S3, the rate performance and cyclic stability of $\text{Li}_{3.33}\text{Cu}_{1.005}\text{Ti}_{4.665}\text{O}_{12}/\text{CuO}$ are better than those of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3.4}\text{Cu}_{0.9}\text{Ti}_{4.7}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CuO}$, which further shows the advantages of this synergistic strategy combining Cu^{2+} substituting and CuO compositing.

References

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- [S2] B.H. Toby, J. Appl. Cryst. 34 (2001) 210–213.