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Research on Atomic-Scale Investigation of Li Storage Mechanism in Spinel $Li_4Ti_5O_{12}$

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Nowadays, there is an increasing need for large-scale energy storage with the developments of renewable energy sources including solar and wind power. Among the candidates, Li-ion batteries have been regarded as one of the most important alternatives to power the electric vehicles (EVs) and/or to store electric energy in large-scale. Nonetheless, the performance of present Li ion batteries can still not meet the requirements for such applications. Spinel $Li_4Ti_5O_{12}$, with zero-strain characteristics and structural stability during charge and discharge process, plays a significant role in long-life Li-ion batteries. However, it is still under dispute on the reaction mechanism, charge compensation and gas-release (possible surface structure) in the $Li_4Ti_5O_{12}$ electrode during cycling. In order to further improve the battery performance, a more fundamental and microscopic understanding on the Li storage mechanism in $Li_4Ti_5O_{12}$ is essential.

Recently, PhD student Xia Lu, Prof. Yong-Sheng Hu *et al.* in Group E01 and Prof. Lin Gu in Group A01, from the Institute of Physics, CAS/ Beijing National Laboratory for Condensed Matter Physics, revealed the full static atomic-scale picture of the spinel anode $Li_4Ti_5O_{12}$ for the first time using the latest spherical aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) as well as the first-principles calculation. Firstly, the Li ions in $Li_4Ti_5O_{12}$ and inserted Li^+ ions can be directly visualized along the [110] direction using STEM-ABF technique (see Figure 1). Secondly, based on this, the two-phase reaction mechanism in this material can be well evidenced by the observation of $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ in the half discharged sample. More importantly, an atomic interfacial structure between two phases was clearly observed, where an almost ideal hetero-interface without any intermediate phase was developed, which is probably related to the zero-strain property of this material as shown in Figure 2. Thirdly, through atomic-scale EELS, the distribution of excess three electrons which are introduced by three Li insertion is inhomogeneous among five Titanium, meaning that three Ti^{4+} transform to Ti^{3+} while the other two keep Ti^{4+}. Finally, it is very interesting to note that we always found that the outmost surface structure with a thickness of 1—2 nm of $Li_4Ti_5O_{12}$ samples is very different from the bulk as shown in Figure 1. This layer is hardly identified and is quite probably related to titanium-rich compositions, which could be responsible for the gas-releasing issues (package swelling) when $Li_4Ti_5O_{12}$ is used as an anode in a real battery. The results were published on *Advanced Materials* (*Adv. Mater.*, 2012, 24: 3233—3238.). Upon publication, the work was immediately highlighted by *Science*.

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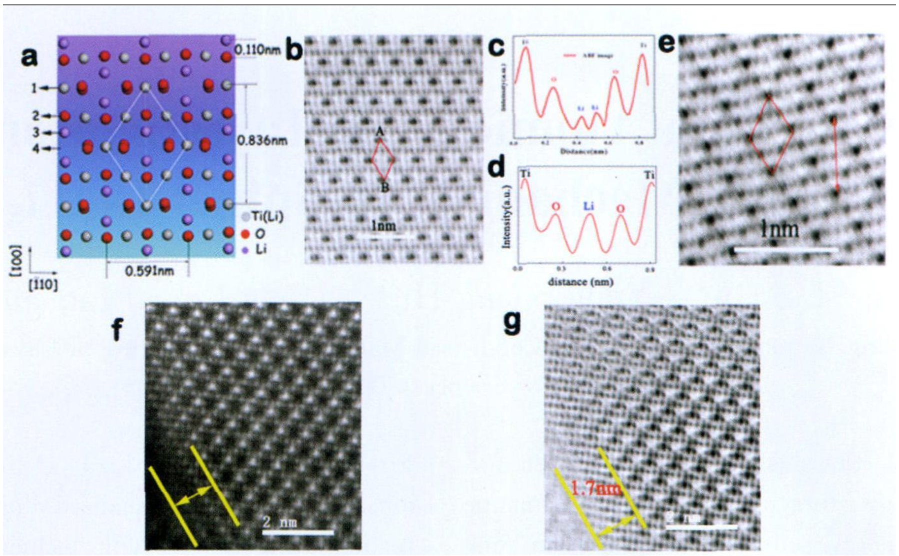

Figure 1. Lattice and STEM images for $Li_4Ti_5O_{12}$ at [110] zone axis. (a) Schematic lattice of $Li_4Ti_5O_{12}$. The numerical labels 1, 2, 3 and 4 in Figure 1a left viewed from [110] direction correspond to the 16d, 32e, 8a and 16c (vacancy) sites in $Li_4Ti_5O_{12}$ lattice. Enlarged ABF images of (b) $Li_4Ti_5O_{12}$ and (e) $Li_7Ti_5O_{12}$ with the corresponding line profile of (c) and (d), respectively. Enlarged HAADF (f) and ABF (g) STEM images of the irregular atomic arrangements in the outmost surface layer of the chemically lithiated $Li_4Ti_5O_{12}$ sample. (Note that in the ABF line profile, image contrast of the dark dots is inverted and displayed as peaks).

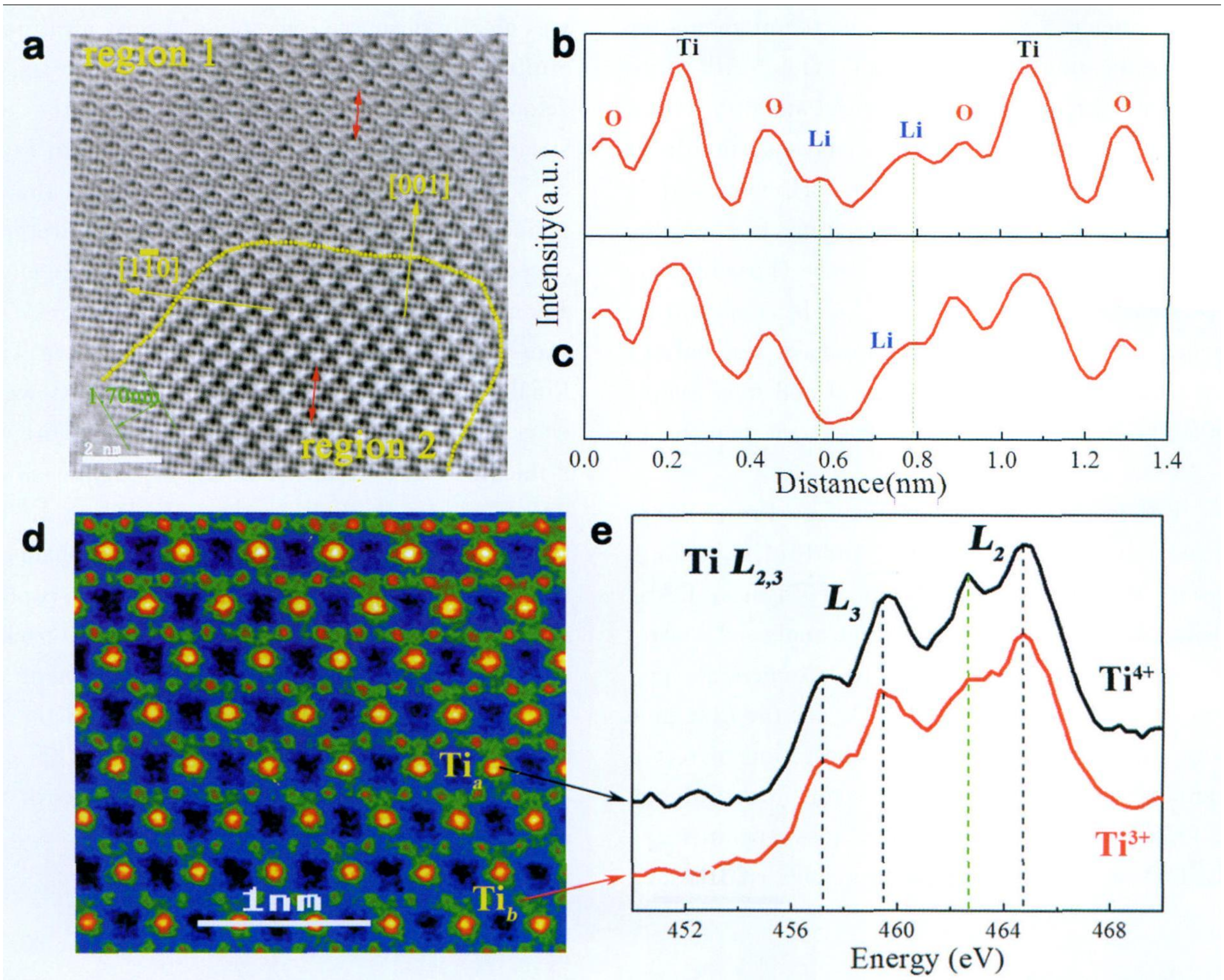

Figure 2. Interfacial structure in chemically lithiated $Li_4Ti_5O_{12}$ sample with about 0.15 mol Li insertion per formula unit at [110] direction. (a) ABF image near the interface between $Li_4Ti_5O_{12}$ phase (region 1) and $Li_7Ti_5O_{12}$ phase (region 2). The yellow dotted line indicates the boundary of the interface. (b) ABF line profile of region 1. (c) ABF line profile of region 2. (d) Color view of the enlarged STEM ABF image with different Ti columns. (e) EELS profile Ti-$L_{2,3}$ edges for the $Li_4Ti_5O_{12}$ electrode when discharged to 1.0 V taken from the two different Ti columns (d) along the [110] direction.

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The link for the paper

1. "Lithium Storage in $Li_4Ti_5O_{12}$ Spinel: The Full Static Picture from Electron Microscopy"

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