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Local Ordering and Lithium Storage in Nanostructured $Li_4Ti_5O_{12}$ Anodes via Scanning Transmission Electron Microscopy

Lijun Wu, Feng Wang and Yimei Zhu

Brookhaven National Laboratory, Upton, New York 11973, USA

The spinel lithium titanate, $Li_4Ti_5O_{12}$ (denoted as LTO), is one promising alternative to graphite as an anode material in lithium-ion batteries due to its excellent cycling ability and safety. Its stable framework allows reversible lithium insertion-de-insertion during electrochemical cycling with little change of lattice parameter. Although it is generally believed that charging/discharging of $Li_4Ti_5O_{12}$ /$Li_7Ti_5O_{12}$ is accomplished by a two-phase equilibrium, direct experimental observation is needed to determine where the lithium goes and its influence on electrochemical properties. However this type of characterization requires high sensitivity to Li and high spatial resolution. Here, we report the local lithium occupancy in the nanostructured LTO using annular bright field (ABF) images which have been demonstrated to be able to visualize Li in atomic resolution [1]. Meanwhile, high angle annular dark field (HAADF) and secondary electron (SE) images are simultaneously acquired to determine the occupancy of Ti atoms in the bulk and near-surface region (Fig. 1a).

LTO possesses a spinel structure where Li atoms occupy all of the 8a sites and 1/6 of the 16d sites, the remaining 5/6 of the 16d sites are taken by Ti atoms, the 32e sites are occupied by O atoms (Fig. 1b). Fig. 1(c) shows a typical morphology of the LTO nanoparticles acquired by SE detector. The nanoparticles exhibit a plate-like shape with plate normal along {110} direction. {111} facets are often observed. The plate size is generally below 100 nm. To obtain information of both heavy and light elements, as well as surface structure from the same area, we acquired ABF, HAADF and SE images simultaneously in the double aberration-corrected JEOL-ARM200F, as shown in Fig. 1(d)-(f). The HAADF image shows Z-contrast due to its large collection angle. The image intensity in the Ti/Li-1 column is much stronger than that in the Ti/Li-2 column because the number of Ti/Li atoms in the former is twice of that in the later (Fig. 1e). The contrast of the O column is weak, while Li is invisible. In contrast, the ABF image shows contrast for heavy elements as well as light elements due to its small collection angle. Both O and Li are visible in the ABF image (Fig. 1(d)). The occupancy of Li at 8a sites is shown by weak contrast in ABF image. Strong contrast of Ti/Li-1 sites in the SE image indicates a Ti-terminated surface.

Fig. 2(a) shows a HAADF image recorded from a near-surface region of a LTO nanoparticle. It is seen that the nanoparticle terminates on {111} Ti/Li plane, with structural re-ordering near the surface. The image of the interior (Fig. 2(b)) shows strong contrast in the Ti/Li-1 column (16d sites), intermediate contrast in Ti/Li-2 column (16d sites), weak contrast in 32e sites, being consistent with the [110] projection of spinel LTO. The image of surface region (Fig. 2(c)) shows strong contrast in all 16d sites, while weak contrast in 32e sites, being consistent with the [110] projection of rock-salt LTO. This implies that the LTO nanoparticles have a heterogeneous structure.

Reference:

[1] Xia Lu *et al*, Adv. Mater. **24**, 3233 (2013).
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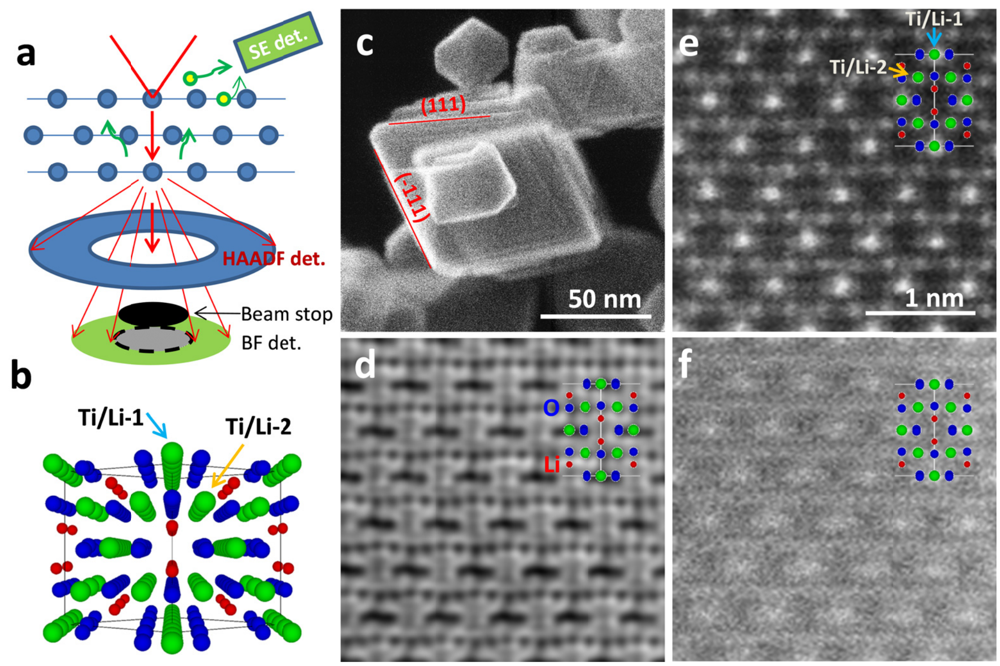

Fig. 1. (a) Schematic of the experimental setup for simultaneous acquisition of high angle annular dark field (HAADF), annular bright field (ABF) and secondary electron (SE) images in scanning transmission electron microscope (STEM). (b) Structure model of $Li_4Ti_5O_{12}$ (LTO) with red, green and blue spheres representing Li, Ti/Li (5/6 Ti + 1/6 Li) and O atoms, respectively. (c) Low magnification SE image of the LTO nanoparticles. (d-f) Simultaneously acquired (d) ABF, (e) HAADF and (f) SE images from the same area. The beam is along [110] direction. The as-acquired ABF image is quite noisy, due to poor signal/noise ratio. The ABF image is slightly processed with a threshold method in frequency space: Fourier transform the acquired image to frequency space, select only points with a high magnitude (e.g. larger than a threshold level) and inverse Fourier transform. The [110] projection of the spinel LTO structure are embedded in the images. The HAADF image shows strong contrast for Ti/Li-1, intermediate contrast for Ti/Li-2, weak contrast for O, while no contrast for Li. The ABF image shows contrast for heavy elements as well as light elements. Li atoms are visible in ABF image.

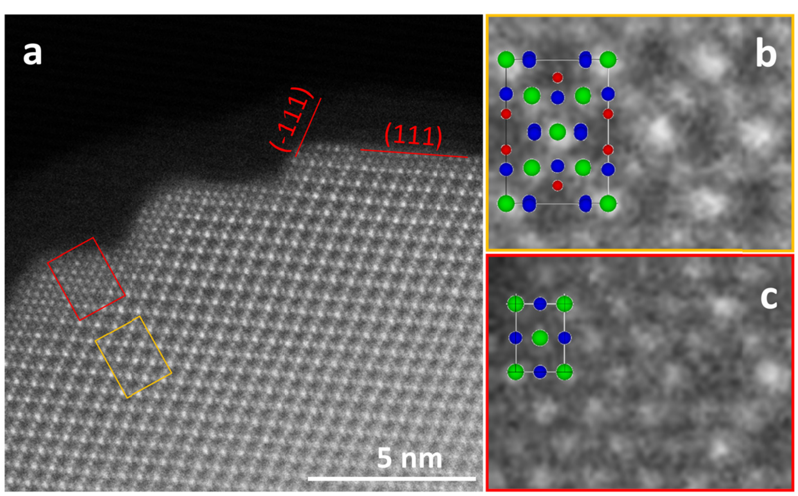

Fig. 2. (a) HAADF image from a LTO nanoparticle, showing the {111} facets. The interior and the edge area marked in (a) are enlarged in (b) and (c), respectively. While the particle has the spinel LTO structure in the interior of the particle, the structure at the edge (surface) has rock-salt LTO structure. The [110] projection of the spinel LTO and rock-salt LTO structures are embedded in the images.

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