

Li K-Edge Spectroscopy Studies of Nanostructured Electrode Materials for Lithium Batteries

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Lithium batteries are the most popular rechargeable storage devices used in portable electronics and will likely be the primary power source for electrical vehicles in the near future [1]. In studying the mechanism of reaction of lithium with electrode materials, NMR and neutron diffraction are powerful techniques capable of probing lithium and its environment, providing access to the local structure and long-range order of the electrodes. But the information is averaged over the big volume of samples, making them not ideal for studies of the nanoelectrodes of high heterogeneity in structure and composition; moreover the study using neutron scattering is still limited to single crystals in most cases. Electron energy-loss spectroscopy in the transmission electron microscope (TEM-EELS) is suitable for studies of nanostructured electrode materials due to its high spatial resolution and sensitivity to light elements (i.e. lithium). However, its full potential has not been well explored because of the weak elastic scattering and high sensitivity to the electron beam of lithium. For example, Li K-edge can be used for mapping the local distribution of lithium and identifying its bonding states provided that optimal measurement conditions can be established [2]. The electron-loss near-edge structure (ELNES) of Li K-edge, due to its sensitivity to the immediate coordination, may also be used to determine the lithium occupancy sites [3, 4].

We report Li K-edge spectroscopy studies of the site occupancy and migration of lithium in the lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), a promising anode material for high cycle-life electrodes [5]. Higher capacities can be achieved by cycling over a wider voltage range, where more than one lithium per redox center is inserted, but lead to a reduced cycle life with reasons as yet unclear. Therefore, a better understanding of where the lithium goes and how it changes the host structure is necessary. As shown in Figure 1, clear evidences of lithium occupancies on both tetrahedral (8a) and octahedral (16d) sites in the initial LTO, and the migration between tetrahedral (8a) and octahedral (16c) sites with lithiation were obtained from the Li K-edge spectra acquired from multiple particles (Fig. 1a-b), in combination with *ab-initio* calculation (Fig. 1c). Excessive Li storage in the surface region was also confirmed from Li K-edge spectra across individual particles (Fig. 1d). The mechanism for the reactions over the full voltage range (between 2.5 V and 50 mV), will be discussed, in accordance with the measure of the bond distortion and charge compensation by a combination of TEM-EELS, synchrotron X-ray diffraction and absorption spectroscopy [6].

References

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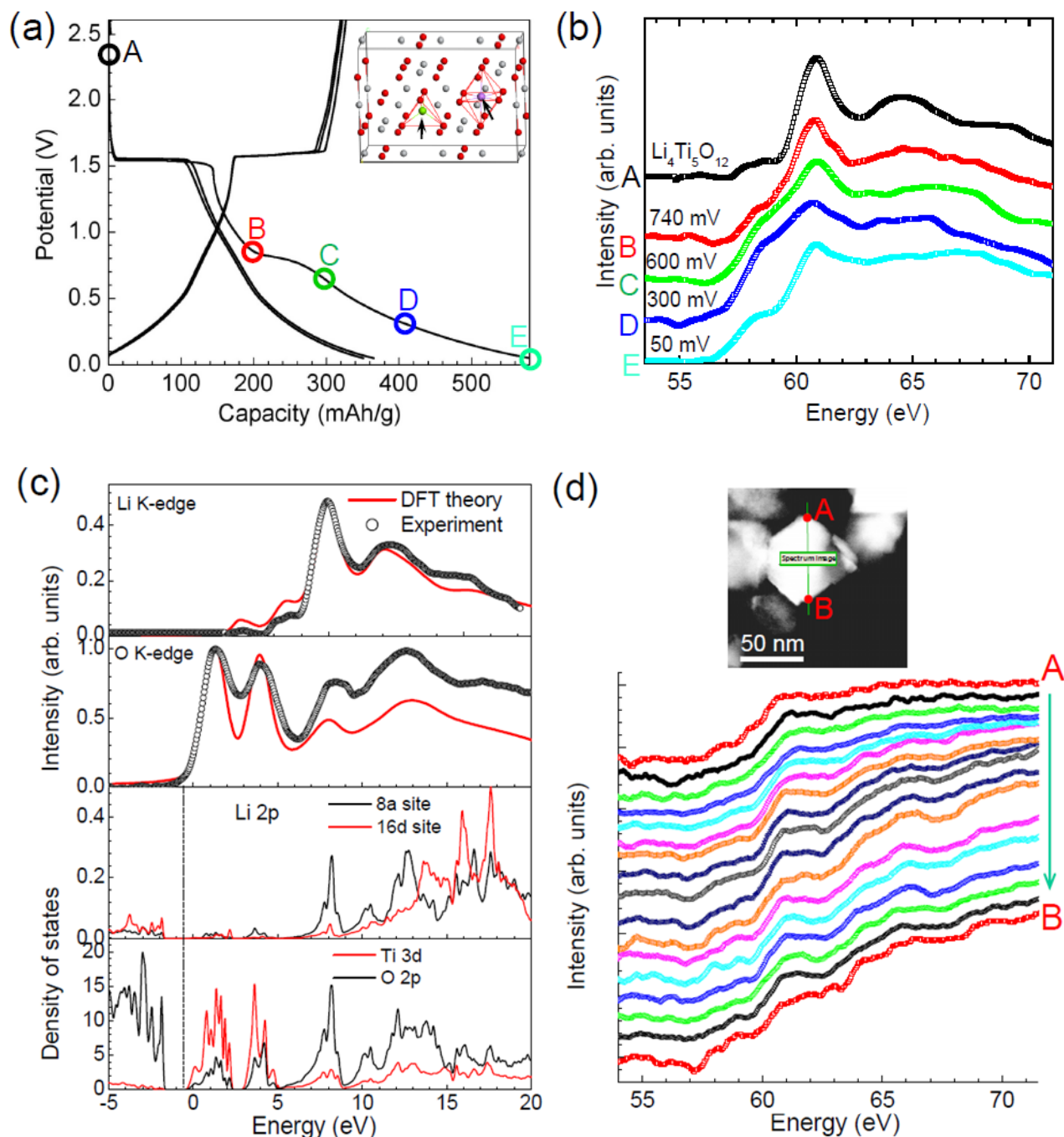


Figure 1. Li K-edge spectroscopy studies of the site occupancy and migration of lithium in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with lithiation over a wide voltage range (2.5 V – 50 mV): a) voltage profile of LTO in the first three cycles, with letters to indicate the samples at certain lithiated states and arrows showing the possible 8a and 16c sites of Li (in the inset); b) Li K-edge spectra at different lithiation states, the variation of the pre-peak showing the lithium migration between 8a and 16c sites; c) calculation of the electronic structure and spectra of the LTO, using the full-potential method via Wien2K code against the experimental data for Li and O K-edges; d) Li K-edge spectra recorded from a single particle lithiated to 600 mV, showing non-uniform intercalation of the Li (i.e. excessive Li storage in the surface region).