

Direct Visualization of Lithium Intercalation in Spinel Iron Oxide by In-Situ Bright-Field Scanning Transmission Electron Microscopy

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In situ transmission electron microscopy (TEM) is a fast-growing area and has attracted tremendous attention in diverse scientific research spanning from materials science to chemistry and biology [1]. Specifically, the advancement of *in situ* TEM in chemically reactive environments has enabled the direct real-time observation of electrochemical reactions in electrode materials for lithium ion batteries [2-4]. Prior *in situ* studies have mostly focused on the electrodes that react with lithium through alloying or conversion reactions, since these processes involve obvious structural and chemical changes that can be readily captured by direct imaging and spectroscopy methods on the nanoscale [2, 3]. On the other hand, the lithium intercalation process as the predominant mechanism of the present battery technology, however, is hard to be tracked due to its insignificant volume change [4]. Here, we present the development of a new strain-sensitive bright-field scanning transmission electron microscopy (BF-STEM) and its implementation of imaging the intercalation reaction during the lithiation of a single magnetite (Fe₃O₄) nanocrystal.

Fe₃O₄ has been widely considered as a promising electrode material because of its ample abundance, non-toxicity, low cost, and high theoretical capacity. We use Fe₃O₄ nanoparticles (~80 nm truncated octahedrons, Figure 1a) with the spinel structure that can accommodate guest Li⁺ ions at the vacant octahedral 16c positions and repel Fe³⁺ cations from tetrahedral 8a to the nearby octahedral 16c sites (Figure 1b). This is an intercalation reaction to cause phase transformation from spinel Fe₃O₄ to rocksalt LiFe₃O₄ (Figure 1c) [5]. Further lithiation will lead to thorough structure destruction to form a composite of metallic Fe and amorphous Li₂O through a conversion reaction (Figure 1d), like in many other transition metal oxides [2]. The entire process of two-step lithiation has also been confirmed by the *in situ* electron diffraction (Figure 1e-g).

Besides the HRTEM imaging to monitor the atomic structure reconstruction, we also demonstrated a new approach to directly visualize the Li intercalation within the entire single nanoparticle using *in situ* BF-STEM on the nanoscale (Figure 2). Comparison between simultaneously acquired HAADF-STEM and BF-STEM images (Figure 2a, b) clearly illustrates the visually distinguishable phase boundary by the contrast arising from the coherent electrons scattered to lower angles, which are more sensitive to a small strain (~1% in this case) induced by negligible volume expansion due to Li insertion. The time-resolved BF-STEM images explicitly show the kinetic evolution of both intercalation and conversion pathways at non-equilibrium conditions. These findings not only elucidate the atomistic mechanism for the two-step lithiation in spinel structured oxides, but also demonstrate a valid methodology for investigating lithium insertion in other intercalation electrode materials or probing strain-sensitive phase transformations in general [6].

References:

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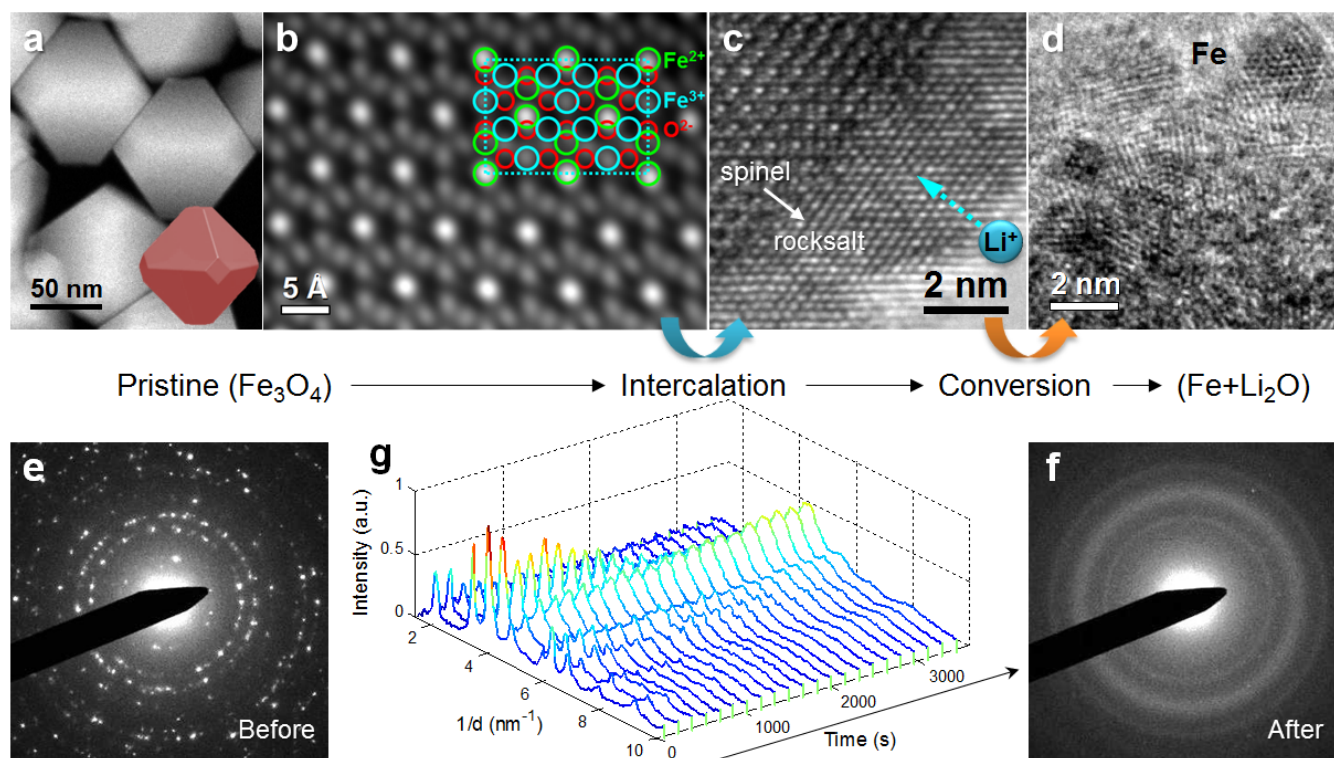


Figure 1. Structural evolution of Fe_3O_4 upon lithiation. (a) Fe_3O_4 nanoparticles in truncated octahedral shape showing (b) spinel structure at the pristine state. (c) Structural reconstruction from spinel to rocksalt as lithiated to form LiFe_3O_4 . (d) Composite of metallic Fe nanocrystallites and amorphous Li_2O after conversion reaction. Electron diffraction patterns (e) before, and (f) after a full lithiation, with (g) time-resolved profiles retrieved from *in situ* electron diffraction to confirm the two-step lithiation.

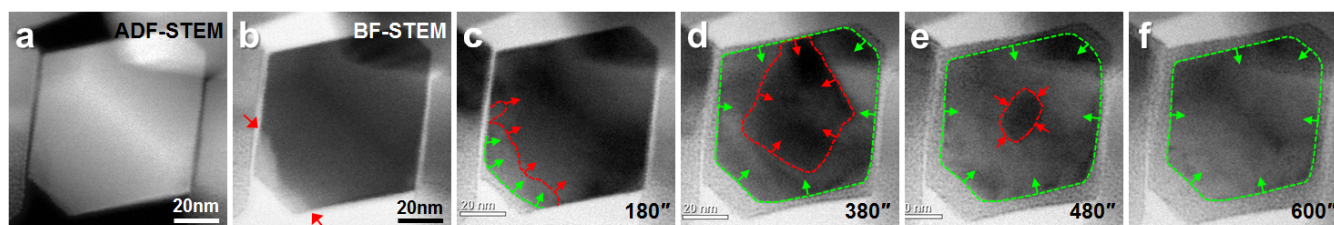


Figure 2. Time-lapsed *in situ* BF-STEM imaging of a single Fe_3O_4 nanoparticle during lithiation. (a) ADF-STEM and (b) BF-STEM images of a same particle showing explicit reaction front in BF-STEM. (c-f) Snapshots at a series of lithiation time to illustrate kinetic evolution of intercalation (red) and conversion (green) reaction pathways.