

# Lithiation/Delithiation Mechanism in LiFePO<sub>4</sub> Cathode Materials

## Revealed by ABF-STEM

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Olivine-type LiFePO<sub>4</sub> is regarded as a promising cathode material for high-power rechargeable lithium-ion batteries, due to its crystal structure stability during charge/discharge cycles, and low cost. However, unlike the conventional LiCoO<sub>2</sub> cathode material, the lithiation/delithiation mechanism of LiFePO<sub>4</sub> is still under debate. Many possibilities have been proposed by different researchers [1]. In this study we directly observed the microstructures of LiFePO<sub>4</sub> nanopowders using a combination of ABF and ADF techniques in a Cs-corrected STEM to shed light on the atomic-scale mechanism/s.

The LiFePO<sub>4</sub> nanopowders were fabricated by a hydrothermal method [2]. An Fe-rich composition was chosen so that the phase separation of LiFePO<sub>4</sub> could be observed. STEM observations were performed on a Cs-corrected JEM-2100F equipped with a Gatan Image Filter (GIF). The minimum probe size of this setup is about 1 Å in diameter. The probe-forming aperture semi-angle was 25 mrad. Detection angles of greater than 52 mrad for annular dark field (ADF) imaging and 6-25 mrad for annular bright-field (ABF) imaging were used.

The as-prepared LiFePO<sub>4</sub> powders consisted of plate-like particles of micron size. Particle thicknesses were about ~100 nm. XRD indicated a pure olivine phase. However, STEM observations showed that phase separation had occurred, as shown in Fig. 1. The matrix contained excess Fe, located on the Li site to form typical anti-site defects. Fig. 2a shows a typical ABF image of the LiFePO<sub>4</sub> matrix. Columns of all four elements, including Li and O, could be observed successfully with atomic resolution. The intensity profile along lines 1 and 2 (Fig. 2b) reveals that the Fe<sub>Li</sub> defects concentrate in layers parallel to the *bc* plane and form an ordered structure in the *a* direction. Such an ordered Fe-rich LiFePO<sub>4</sub> phase is metastable and separates into stoichiometric LiFePO<sub>4</sub> and FePO<sub>4</sub> phases. Based on these microstructural observations, we propose a detailed lithiation/delithiation mechanism. The study demonstrates that STEM is a powerful tool for revealing atomic-level phenomena in Li- and other low-element-containing materials with unprecedented clarity [3].

## References

- [1] L. Yuan et al., *Energy Environ. Sci.*, 4 (2011) 269.
- [2] S. Yang et al., *Electrochem. Commun.*, 3 (2001) 505.
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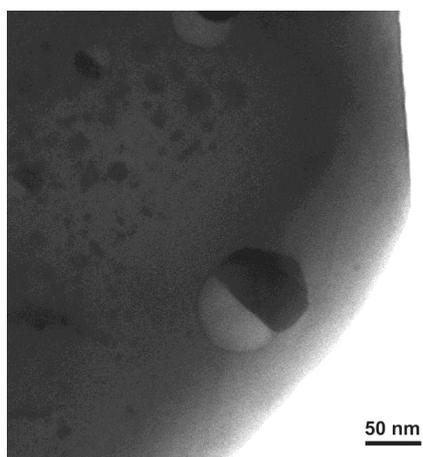


FIG. 1. BF-STEM image of an LiFePO<sub>4</sub> particle showing microscopic phase separation.

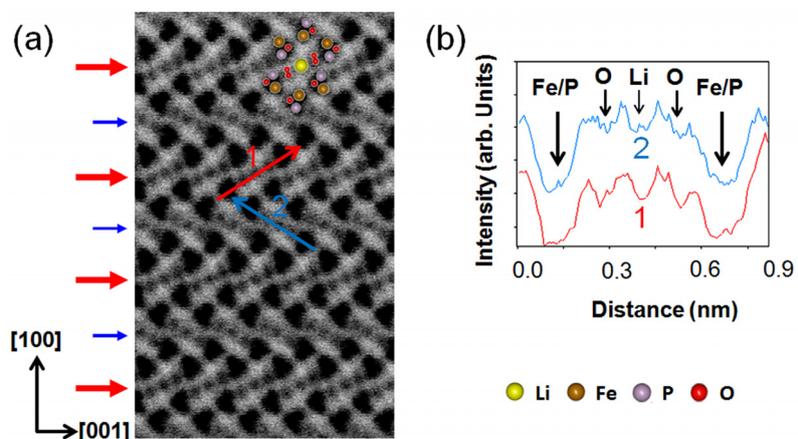


FIG. 2. (a) Typical ABF image of the LiFePO<sub>4</sub> matrix and (b) intensity profiles along lines 1 and 2