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Introduction

Lithium iron phosphate (LiFePO₄) is a well-studied compound with a lot of promise as cathode material in rechargeable batteries. Due to low cost, low toxicity, safety and the abundance of iron LiFePO₄ is considered a very attractive energy storage option for the automotive industry.

To better understand the lithium deintercalation process we performed Selected Area Electron Diffraction (SAED) experiments and High-Resolution integrated Differential Phase Contrast Imaging (iDPC) on electrochemically (de)lithiated LiFePO₄. Single particle diffraction experiments and iDPC imaging enable us to successfully determine individual phases and the quantitative degree of delithiation.

In SAED lateral resolution is limited at 50 nm due to our selected area aperture diameter. For HR-STEM/iDPC that restriction does not apply. We can therefore obtain HR-FFTs to measure the local crystal lattice constants. While SAED provides very high precision, using the lattice constant ratios enables a quantitative comparison of SAED and HR-STEM/iDPC results even between various microscopes.

Results

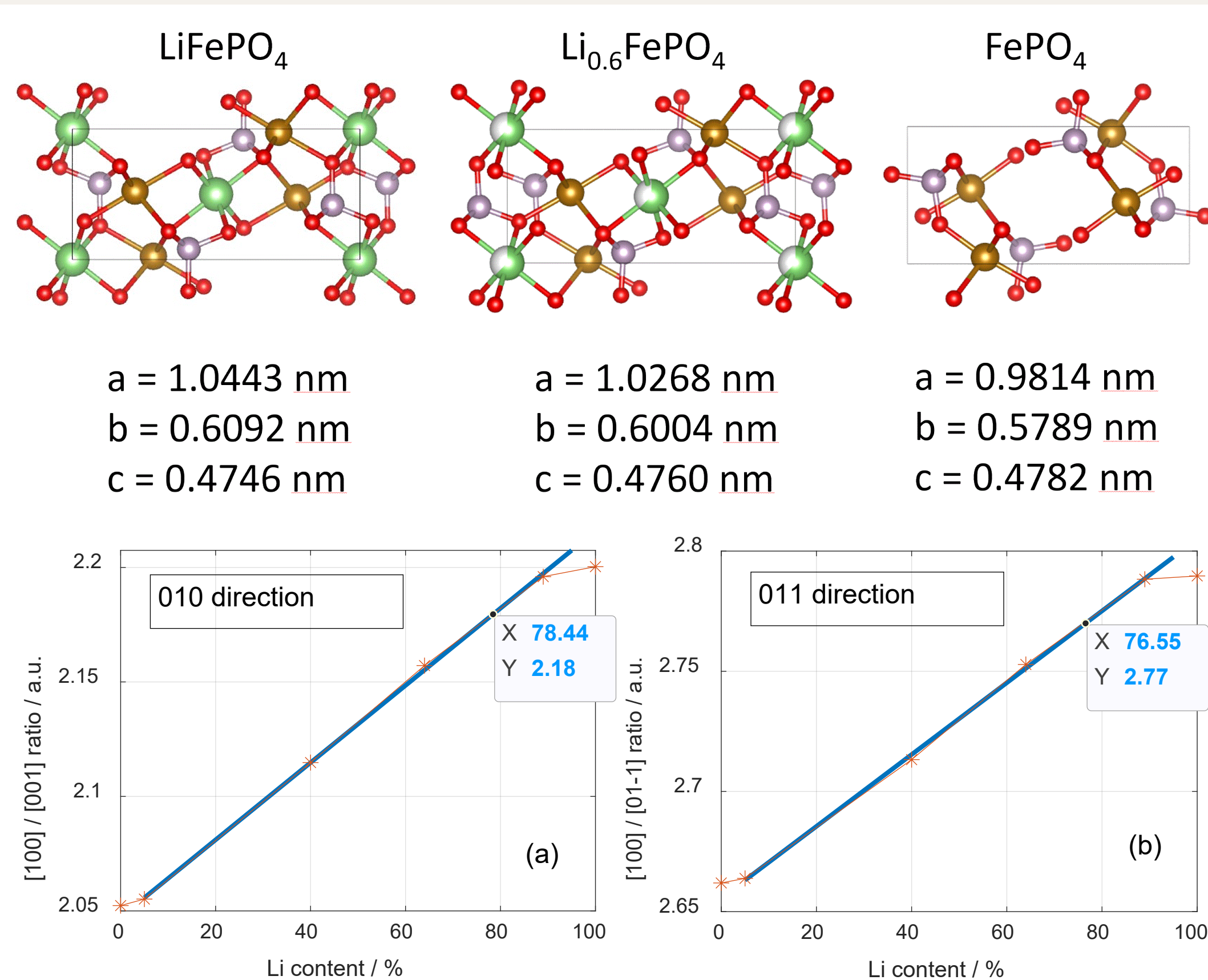


Figure 1: LiFePO₄ [2], Li_{0.6}FePO₄ and FePO₄ reference models [3]. The ratio of the lattice constants changes linearly with delithiation. Example calculations are carried out for the diffraction patterns in figure 2.

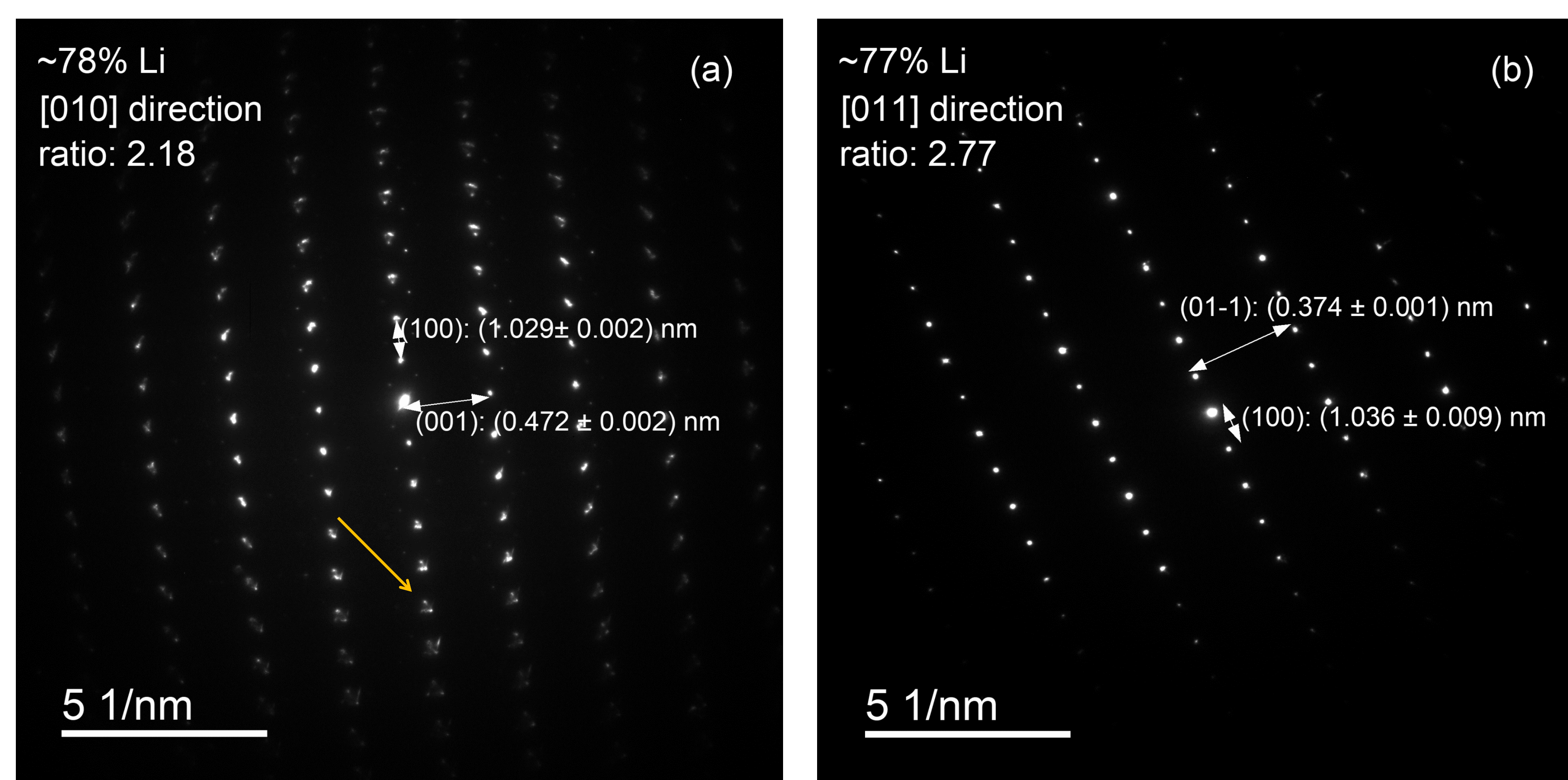


Figure 2: SAED pattern (a) of a single (L)FP crystal. The arrow indicates the presence of three phases, two of which are FePO₄, and another Li_{0.78}FePO₄. A second diffractogram (b) of a different particle showing one phase of Li_{0.77}FePO₄. The lattice constant ratios specify the respective delithiation grade as seen in figure 1 (a) and (b)

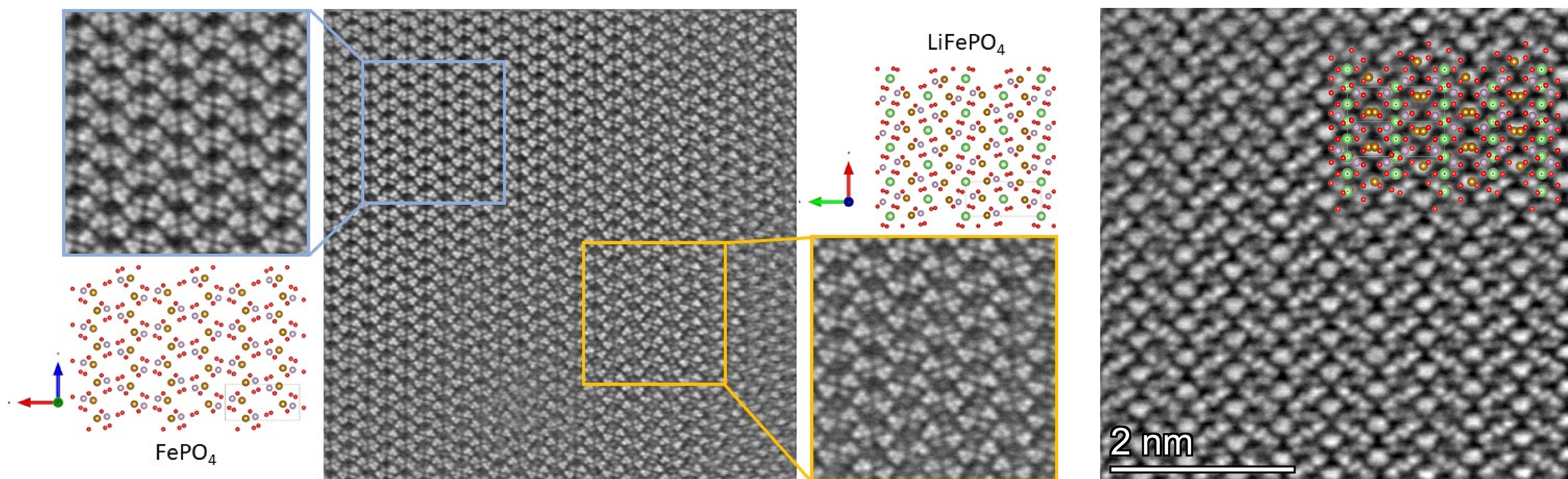


Figure 3: HR-iDPC image (a) of phase boundary in (L)FP in [010] direction. A gradually increasing lithiation is observed from the upper left to the lower right. Another crystal in [011] direction is shown in (b). Partial delithiation is observed across the whole image, with Li-Positions showing varying contrast and empty spots.

Conclusion

SAED is a useful and viable method for phase identification of Li_xFePO₄. Partial delithiation can even be measured quantitatively comparing lattice constant ratios with reference models. These results are confirmed and reproduced with atomically resolved STEM and iDPC.

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References/ Literature

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