

## Interface and Surface Local Atomic Structures of Lithium Ion Battery Oxides

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The properties of lithium ion battery (LIB) cathodes strongly depend on the diffusion of lithium ions during charge/discharge process. Since this behavior determines the stability, lifetime and reliability, direct visualization of lithium site is required to understand the mechanism of the diffusion of lithium ions. Aberration corrected STEM is very powerful imaging technique to directly observe the atomic columns inside a crystal. In this study, aberration corrected HAADF and ABF STEM are applied to directly observe the interface and the surface of the olivine  $\text{Li}_x\text{FePO}_4$  and delithiated olivine ( $\text{FePO}_4$ ) [1,2], and the mechanism of the lithiation/delithiation is discussed based on the observation results.

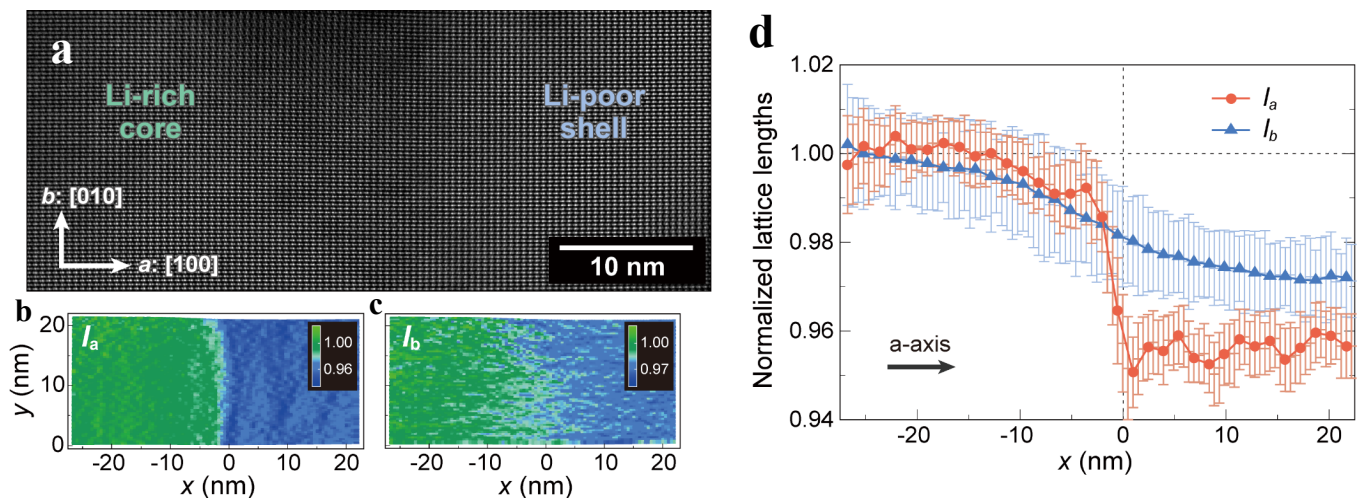
For the cathode of  $\text{LiFePO}_4$ , previous studies showed that the lithiation/delithiation in  $\text{LiFePO}_4$  is basically the two-phase process, that is,  $\text{LiFePO}_4/\text{FePO}_4$  interfaces propagate through the bulk region with inserting/extracting lithium.  $\text{LiFePO}_4$  powders were used to introduce the phase boundaries, and the chemical delithiation was conducted ( $\text{NOBF}_4$ ) in acetonitrile solvent for the powders. TEM observations showed that the average particle size is of the order of  $\mu\text{m}$ , and most particles have core-shell structures. Fig.1(a) shows the integrated HAADF STEM image of the phase interface between the core and shell regions, which shows the formation of coherent interface [3]. Fig.1 (b, c) shows the lattice variation maps obtained by Gaussian fittings. It is found that the phase interface is parallel to the  $\{100\}$  plane. A comparison between parts (b) and (c) of Fig.1 shows that the lattice variation widths are highly orientation-dependent. This feature is also highlighted in the line profiles of these maps calculated along the a-axis direction (Fig.1 (d)). The  $l_a$  shows a narrow variation width, less than 10 nm, whereas the change of  $l_b$  is gradual and extends over 30 nm. Since  $l_a$  is perpendicular to the interface plane, it can be relaxed without severe limitations of lattice coherency across the interface. On the other hand,  $l_b$  is parallel to the interface and its variation must proceed gradually to elastically sustain the lattice mismatches. The two phase interface is thus found to have very complicated feature, which is related to the lithiation/delithiation mechanism.

In order to understand the surface reconstruction during lithiation/delithiation, the (010)  $\text{LiFePO}_4$  surfaces was directly observed by STEM [4]. Commercially available  $\text{LiFePO}_4$  single crystals (Oxide Co., Japan) were used for all experiments. Crystals were cut perpendicular to their (010) axis and polished, and the structures of (010) surfaces before and after chemical delithiation were characterized by STEM. Fig. 2 (a) shows ABF STEM image of a pristine (010) surface with the incident beam parallel to the [001] direction. The surface is atomically flat, which indicates that it has a low energy and high stability. It was found that P and Fe atom columns undergo comparatively large displacements near the surface as shown in Fig. 2 (b), which was consistent with the results from first-principles calculations, shown in Fig. 2 (c). The magnitudes of the P and Fe displacements were also found to depend on the location of the outmost Li sites. After chemical delithiation, a number of microcracks formed as a consequence of the large difference in volume between  $\text{LiFePO}_4$  and  $\text{FePO}_4$ . Li ions were found to migrate back to surface regions after the partial delithiation, showing the facile nature of Li transport in the [010] direction. It was confirmed that the crystal had returned to a single  $\text{Li}_{1-\alpha}\text{FePO}_4$  phase after 3000h. These results are consistent with phase

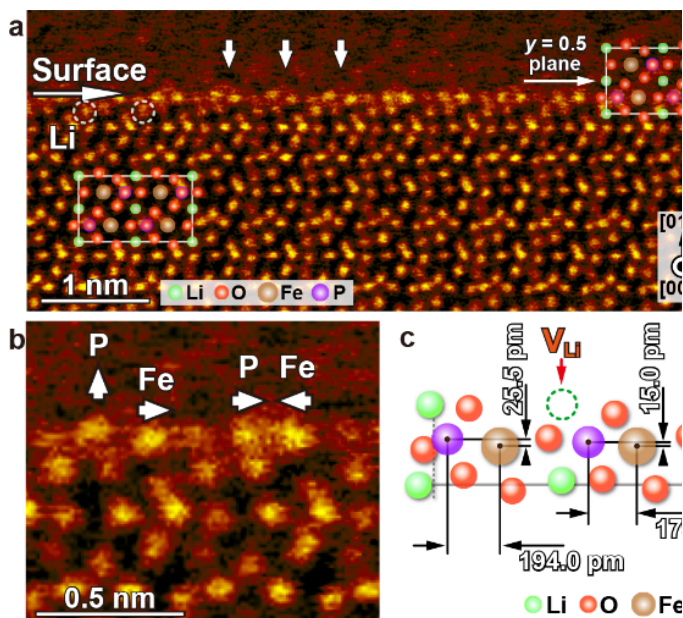
transformation models involving metastable phase formation and relaxation, and provide atomic-level insights into the fundamental mechanism [5].

#### References:

- [1] S. D. Findlay *et al*, *Microscopy*, **66** (2017), p. 3.  
 [2] R. Huang and Y. Ikuhara, *Curr. Opin. Sol. Stat. & Mat. Sci.* **16** (2012), p. 31.  
 [3] A. Nakamura, *et al*, *Chem. Mater.*, **26** (2014), p. 6178.  
 [4] S. Kobayashi *et al*, *Nano Lett.* **16** (2016), p. 5409.  
 [5] A part of this work was supported by the Research & Development Initiative for Scientific Innovation of New Generation Batteries II (RISING II).



**Figure 1.** (a) Integrated HAADF STEM image of the phase interface. Two-dimensional maps of the normalized lattice lengths for the (b)  $a$ -axis ( $l_a$ ) and (c)  $b$ -axis ( $l_b$ ). (d) Line profiles of each lattice variation calculated along the  $a$ -axis direction. Error bars indicate the standard deviations at each point.



**Figure 2.** (a) ABF STEM image of the (010) surface of  $\text{LiFePO}_4$ . (b) Magnified ABF STEM image. The white arrows indicate the directions of shift of P and Fe atom columns. (c) Cross-sectional model of the reconstructed (010) surface of  $\text{LiFePO}_4$  obtained by first-principles calculations.