Supporting Information

Atomic-Scale Analysis of Biphasic Boundaries in the Lithium-Ion Battery Cathode Material LiFePO₄

Shunsuke Kobayashi,^{*,†}Akihide Kuwabara,[†] Craig A. J. Fisher,[†] Yuichi Ikuhara^{†,‡} [†]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Atsuta, Nagoya 456-8587, Japan [‡]Institute of Engineering Innovation, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan *Corresponding author E-mail:s_kobayashi@jfcc.co.jp

1. The partially delithiated LiFePO₄ crystal

Figures S1a and S1b show SEM images of the cleaved LiFePO₄ surface. A (h01) surface similar to that highlighted in Fig. S1b was selected and prepared as a TEM specimen using FIB. Figure S1c shows schematic models of how the (h01) surface and phase boundary of the specimen were affected by delithiation, noting that Li migration occurs predominantly one-dimensionally parallel to the *b* axis in LiFePO₄.



Figure S1. (a) SEM image of the surface of an LiFePO₄ single crystal viewed from [100] zone axis after cleaving.
(b) Magnified view of SEM image of a cleaved LiFePO₄ surface. (c) Schematic of relationship between (h01) surface and Li migration direction.

Figure S2a shows a low-magnification BF STEM image of the LiFePO₄ crystal after partial chemical delithiation; Figs. S2b and S2c show electron diffraction patterns taken from single-phase regions of LiFePO₄ and FePO₄, respectively; Fig. S2d shows electron diffraction patterns obtained at the interface between the end-member phases; and Fig. S2e shows an electron diffraction pattern from the near-(201) surface. The pattern in Fig. S2d contains two evenly shaped, round spots corresponding to FePO₄ and Li_{x≈1}FePO₄, whereas the pattern in Fig. S2e contains one round spot and one elongated spot, the latter corresponding to the intermediate phase Li_xFePO₄ (0.3 < x < 0.8), whose lattice parameters vary gradually as a result of its uniform Li-ion concentration gradient. The pattern in Fig. S2e thus indicates that the near-(201) surface of the delithiated crystal is capped by a narrow region (≈ 20 nm thick) of the intermediate phase.



Figure S2. (a) A low-magnification BF STEM image of the near-(201) surface of an LiFePO₄ crystal after partial chemical delithiation. (b-e) Selected area electron diffraction patterns of the (b) LiFePO₄ phase, (c) FePO₄ phase, (d) biphase boundary, and (e) surface region, taken from the areas enclosed by red circles in (a) labelled A, B, C, and D, respectively.

2. Artifacts in Li column contrast in ABF STEM images

Annular bright-field (ABF) imaging in scanning transmission electron microscopy (STEM) has developed rapidly to become a powerful technique for detecting columns of light elements, e.g., oxygen and lithium, and (under the right conditions) their vacancy contents.¹ ABF STEM, however, is liable to produce artifacts, especially where light elements are concerned.²⁻³ These factors are important in the case of LiFePO₄ because arguably the most important element, Li, is the lightest metal element, and in this work we show that even a small deviation of the incident electron beam from exact alignment with the desired zone axis can produce artifacts because ABF contrast is dominated by elastically scattered electrons.⁴ Indeed, the appearance of artifacts in ABF-STEM intensities of Li columns as a result of small misalignments between electron beam and atom columns in the case of LiFePO₄ has occasionally led to incorrect interpretation of the data.

The large coherency strain field in the vicinity of the biphasic interface in effect means that slight distortion to the crystal lattice as a function of distance from and across the interface is unavoidable, and thus in practice it is impossible to keep the electron beam exactly aligned along the same zone axes of the different phases simultaneously. This makes it difficult to avoid image artifacts and determine the position of each atom column precisely. To measure Li-ion concentrations quantitatively, especially near boundaries between Li-rich and Li-poor phases, alternative techniques thus need to be developed that are insensitive to the degree of misalignment between electron beam and atom columns.

Figure S3a shows the ABF STEM image corresponding to Fig. 2d in the main text. The contrast in the image changes near the boundary between $\text{Li}_{\approx 0.6}\text{FePO}_4$ and $\text{Li}_{\approx 0.1}\text{FePO}_4$ phases. The periodicity in this change in column contrast in the [100] direction can be seen in the Li column intensity map in Fig. S3b. A higher-magnification ABF STEM image and Li column intensity map are shown in Figs. S3c and S2d, respectively, and the intensity profiles in Fig. S3e, obtained from regions A1-A2 and B1-B2 in Fig. S3c, show the changes in intensity of Li columns quantitatively. These results appear to suggest that the structure has undergone *bc* staging.

However, Li column intensities in ABF STEM images of LiFePO₄ are strongly affected by imaging conditions, so that changes in Li column intensities are not necessarily a reflection of the intrinsic structure; although ABF imaging is an extremely useful method for observing light elements such as oxygen and lithium, changes in column intensity may be an artifact of the conditions used for ABF imaging.²⁻³ For example, the periodic variation in contrast in the ABF STEM images in Fig. S3b can be explained by crystal tilting effects, namely, electron beam/atom column misalignment.



Figure S3. (a) ABF STEM image of the region between $FePO_4$ and the intermediate phase near the (201) surface corresponding to Fig. 2d in the main text. (b) The ABF STEM image in (a) with a superimposed Li column intensity color map. (c) A magnified view of the region enclosed by the rectangle in (a). (d) The ABF STEM image in (c) overlaid with an Li column intensity map using the same color scale as in (b). (e) ABF intensity profiles for Li columns along rows A1-A2 and B1-B2 in (c).

To quantify the effect of beam misalignment, we examined changes in Li column intensities in LiFePO₄ viewed down the [010] zone axis after introducing small deviations R_a and R_c about *a* and *c* lattice directions (Figs S4a) using ABF STEM image simulations. For example, four tilt conditions for rotations $R_a = 0$ or 0.5° and $R_c = 0$ or 0.5° are illustrated in Fig. S4b. Figure S5a shows the simulated ABF STEM images for rotations of 0 to 1 degrees. For large misalignments, i.e., $R_a = 1^\circ$ and/or $R_c = 1^\circ$, the atomic structure is no longer visible in the ABF image. Figure S5b shows the 9 simulated images overlaid with maps of the Li column intensities for rotations up to 0.5°. When R_a and R_c are between 0.2 and 0.5°, Li column intensities appear to have a double periodicity when measured along [100]. Figure S5c shows a magnified view of the ABF image for $R_a = 0.2$ and $R_c = 0.5$. Intensity line profiles in Fig. S5e measured along lines A1-A2 and B1-B2 in Fig. S5c should be almost the same in the (compositionally uniform) Li-rich phase, but instead show marked differences.

These results indicate that periodic contrast in experimental ABF STEM images (Fig. S3b) may be an artifact caused by small but unavoidable crystal misalignment between electron beam and atom column. This conclusion is reinforced by that the fact that quantitative HAADF image analysis did not reveal any periodic structures but rather indicated that Li ions are randomly distributed. Further details are provided in the next section. To summarize, our systematic image simulations indicate that ABF STEM imaging of LiFePO₄ can lead to incorrect interpretations of the crystal structure because of small deviations of the electron beam from the "true" zone axis. This is likely to be especially true at the interface between Li-rich and Li-poor phases because the coherency strain in the crystal leads to distortions from orthorhombic symmetry to non-orthogonal symmetries such as monoclinic or triclinic.



Figure S4. (a) Schematic image of relationship between crystal orientation and electron beam direction used in image simulations. (c) The unit cell of LiFePO₄ viewed with different amounts of deviation (tilts) from the [010] zone axis.



Figure S5. (a) ABF STEM image simulations with varying amounts of deviation from the [010] zone axis of LiFePO₄ for the rotation axes shown schematically in Fig. S4a. The sample thickness was set to around 15 nm. (b) ABF STEM images for R_a and R_c between 0 and 0.5 overlaid with maps of Li column intensity differences, $I_{Li} - I_{Li}^{min}$, where I_{Li}^{min} is the minimum Li column intensity in the image. (c) A magnified view of the simulated ABF STEM image for $R_a = 0.2$ and $R_c = 0.5^\circ$; (d) the image in (c) overlaid with its columnar intensity difference map. (e) ABF intensity profiles spanning a single Li column along rows A1-A2 and B1-B2 in (c).

3. Quantitative analysis of Li concentrations using HAADF STEM

HAADF STEM is less prone to generating artifacts than annular bright-field imaging (as explained in section 2 of Supporting Information), and produces directly interpretable images whose intensities scale with the total atomic number, Z, of an atom column (approximately as Z squared).⁵ Despite Li columns not being detectable directly in HAADF mode, our method allows Li-ion concentrations of individual columns to be quantified by measuring the local strain around neighboring Fe (Z = 26) columns, which are visible as strong bright contrast. HAADF STEM is less prone to image artifacts than ABF STEM, but artifacts resulting from misalignment of the incident electron beam are still possible, so we carefully checked the sensitivity of HAADF images to beam misalignment using image simulations.

In the case of LiFePO₄, there are two distinct Fe-Fe distances when viewed down the [010] axis, namely those between Fe1 and Fe2 ions, labeled d_a , and those between Fe3 and Fe4 ions, labeled d_b , in the unit cell shown in Fig. S6. We evaluated the sensitivity of HAADF STEM images to crystal tilting quantitatively by measuring Fe-Fe distances of d_a and d_b , for different amounts of rotation about *a* and *c* axes of the LiFePO₄ olivine unit cell in Fig. S4a.



Figure S6. Schematic diagrams showing d_a and d_b distance between Fe ions in structure models of orthorhombic Li_xFePO₄ viewed down <010> zone axes.

Figure S7a shows simulated HAADF STEM images for different rotations R_a and R_c , confirming that the crystal structure (atom columns) of LiFePO₄ can be identified up to rotations of 0.5°. Figures S7b and S7c show Fe-Fe distance maps of d_a and d_b , respectively, for each of the simulated images. The maps highlighted by red frames in Figs. S7b and S7c show marked differences in their Fe-Fe distances to the other maps, giving the appearance of a periodic structure in the [100] direction. The maps also show that the effect of crystal tilting is much smaller in the case of d_a than d_b .



Figure. S7 (a) Simulated HAADF STEM images for different amounts of deviation from the [010] zone axis of LiFePO₄. Rotation directions are the same as those illustrated in Fig. S3a. Fe-Fe distance maps from HAADF STEM images in (a): (b) d_a , and (c) d_b . Colors in (b) and (c) indicate δd_a , the difference between d_a and its overall minimum value (d_a^{min}), and δd_b , the difference between d_b and its overall minimum value (d_b^{min}). Numerical values in the STEM images in (b) and (c) are maximum differences δd_a^{max} and δd_b^{max} , respectively.

The effect of tilting can be appreciated more readily if a much larger tilt angle is applied. Figures S8a and S8b show the unit cell of LiFePO₄ viewed directly down the [010] zone axis and when tilted by 10° around *a* and *c* axes. When the electron beam and crystal are perfectly aligned (Fig. S8a), Fe-Fe distances d_a and d_b are identical, as in Fig. S6. In contrast, when the crystal is tilted relative to the incident beam, two measurably different values of Fe-Fe distance d_b become apparent in the projected image, labelled, d_{b1} and d_{b2} , because Fe-Fe vectors are inclined relative to the rotation axes. In the case of d_a , however, splitting of the projected distances into d_{a1} and d_{a2} is less severe because the displacement vectors are more-or-less parallel to each other, and thus vary by the same amount when the crystal is rotated.

Experimentally, crystal tilts are typically at most 0.2 degrees. Rotating the crystal by $R_a = R_c = 0.2^\circ$ produces a difference between d_{a1} and d_{a2} of about 2 pm (as in Fig. S7a). In terms of Li content x in Li_xFePO₄, this corresponds to a change in x of $\Delta x \approx 0.05$, which is within the error range of this analysis method. This analysis shows that measuring d_a in HAADF STEM images minimizes the effect of artifacts caused by beam/crystal misalignment thereby allowing the Li concentration of each column to be estimated reliably.



Figure S8. Crystal models of LiFePO₄ with (a) $R_a = 0$ and $R_c = 0$, i.e., perfect alignment down the [010] zone axis; and (b) $R_a = 10^\circ$ and $R_c = 10^\circ$, i.e., large beam/crystal misalignment. Solid and dotted blue lines indicate distances d_{a1} and d_{a2} , respectively. Solid and dotted red lines indicate distances d_{b1} and d_{b2} , respectively.

We used the same quantitative analysis method to examine the effect of crystal tilting on STEM images of $Li_{0.5}FePO_4$ with either a monoclinic structure or a *bc* staging structure (Fig. S9a-f). Figure S9b shows simulated ABF STEM images overlaid with Li column intensity maps for deviations from the [010] zone axis of monoclinic $Li_{0.5}FePO_4$ by rotations R_a and R_c . The Li column intensities in the image with $R_a = R_c = 0.2^\circ$ contain artifacts that give the appearance of a periodic structure along [100]. In contrast, the simulated HAADF STEM images in Fig. S9c with the same amount of crystal misalignment do not contain any periodic artifacts. These results confirm that HAADF imaging down [010] can be used reliably to determine if $Li_{0.5}FePO_4$ has a monoclinic structure with randomly distributed Li ions or not, even in the presence of (slight) beam misalignment. In the case of $Li_{0.5}FePO_4$ with the *bc* staging structure illustrated in Fig. S9d, both ABF (Fig. S9e) and HAADF (Fig. S9f) images contain periodic contrast in the [100] direction regardless of whether the crystal is tilted or not. Although the effects of electron beam channeling and lens aberrations need to be taken into account for a more rigorous explanation of the effect of crystal tilting on image contrast, the above results show that quantitative HAADF image analysis can also be used reliably to detect *bc* staging in the intermediate phase.



Figure S9. (a) Structure model of monoclinic $Li_{0.5}FePO_4$ used in image simulations. (b) Simulated ABF STEM images of monoclinic $Li_{0.5}FePO_4$ for different crystal tilts R_a and R_c overlaid with difference intensity spots. (c) Simulated HAADF STEM images of monoclinic $Li_{0.5}FePO_4$ for different crystal tilts R_a and R_c with Fe-Fe distance d_a maps overlaid on their right-hand sides. (d) Structure model of $Li_{0.5}FePO_4$ with *bc* staging used in image simulations. (e) Simulated ABF STEM images of monoclinic $Li_{0.5}FePO_4$ for different crystal tilts R_a and R_c overlaid with difference intensity spots. (f) Simulated HAADF STEM images of monoclinic $Li_{0.5}FePO_4$ for different crystal tilts R_a and R_c overlaid tilts R_a and R_c overlaid with difference intensity spots. (f) Simulated HAADF STEM images of monoclinic $Li_{0.5}FePO_4$ for different crystal tilts R_a and R_c overlaid with Fe-Fe distance d_a maps on their right-hand sides. The zone axis is [010] in both cases.

4. Crystal systems used in DFT calculations of Li_xFePO₄

Table S1 . Formation enthalpies of Li_xFePO_4 ($x = 0.25, 0.5, 0.67, 0.75$) using different U_{eff} parameter
and the Li-ion and vacancy configurations in Figure 5 of the main manuscript.

$U_{(aV)}$	Formation enthalpy, $\Delta H_{\rm f}$ (meV)					
U _{eff} (ev)	Li _{0.25} FePO ₄	Li _{0.5} FePO ₄	Li _{0.67} FePO ₄	Li _{0.75} FePO ₄		
4.3	11.2	7.3	2.0	5.2		
3.7	10.6	7.3	4.1	5.0		
4.9	10.9	6.7	3.1	4.8		

Table S2. Calculated lattice parameters of Li_xFePO₄.

	FePO ₄	Li _{0.25} FePO ₄	Li _{0.5} FePO ₄	Li _{2/3} FePO ₄	Li _{0.75} FePO ₄	LiFePO ₄
Lattice Type	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space Group	Pnma	$P\overline{1}$	$P2_{1}/m$	$P2_{1}/n$	$P\overline{1}$	Pnma
<i>a</i> (Å)	9.98424	4.84436	4.81666	11.99525	4.77882	10.43905
<i>b</i> (Å)	5.92793	11.76699	11.89016	18.02909	12.00686	6.07051
<i>c</i> (Å)	4.88483	11.92258	11.98177	4.79356	12.04723	4.74151
α (°)	90	59.3907	59.3992	90	59.5415	90
β (°)	90	90.3217	90	90	89.9963	90
γ (°)	90	90.5213	90	120.6167	89.9617	90
Vol. (Å ³)	289.11	584.90	590.64	892.15	595.86	300.47

Table S3. Calculated lattice parameters of Li_{0.5}FePO₄ with *ac* and *bc* staging.

Li _{0.5} FePO ₄	ac staging	<i>bc</i> staging
Lattice Type	Monoclinic	Monoclinic
Space Group	$P2_{1}/c$	$P2_{1}/m$
<i>a</i> (Å)	10.13404	10.08372
<i>b</i> (Å)	6.03085	5.99118
<i>c</i> (Å)	4.84174	4.85278
α (°)	90	90
β (°)	90	88.0485
γ (°)	90.6372	90
Vol. (Å ³)	295.89	293.00



Figure S10Lattice volume per formula unit versus Li content, *x*, using data in Table S1.



Figure S11 Structure models of $Li_{0.5}$ FePO₄ with (a) *ac* staging, and (b) *bc* staging, each viewed from two orthogonal directions.

References

- Findlay, S. D.; Huang, R.; Ishikawa, R.; Shibata, N.; Ikuhara, Y., Direct Visualization of Lithium via Annular Bright Field Scanning Transmission Electron Microscopy: a Review. *Microscopy (Oxf)* 2017, *66*, 3-14.
- 2. Findlay, S. D.; LeBeau, J. M., Detector Non-Uniformity in Scanning Transmission Electron Microscopy. *Ultramicroscopy* **2013**, *124*, 52-60.
- Gao, P.; Kumamoto, A.; Ishikawa, R.; Lugg, N.; Shibata, N.; Ikuhara, Y., Picometer-Scale Atom Position Analysis in Annular Bright-Field STEM Imaging. *Ultramicroscopy* 2018, *184*, 177-187.
- Findlay, S. D.; Shibata, N.; Sawada, H.; Okunishi, E.; Kondo, Y.; Ikuhara, Y., Dynamics of Annular Bright Field Imaging in Scanning Transmission Electron Microscopy. *Ultramicroscopy* 2010, *110*, 903-23.
- 5. Pennycook, S. J.; Jesson, D. E., High-resolution Z-contrast imaging of crystals. *Ultramicroscopy* **1991**, *37*, 14-38.