Correlative image learning of chemo-mechanics in phase-transforming solids

Haitao D. Deng, Hongbo Zhao, Norman Jin, Lauren Hughes, Benjamin H. Savitzky, Colin Ophus, Dimitrios Fraggedakis, András Borbély, Young-Sang Yu, Eder G. Lomeli, Rui Yan, Jueyi Liu, David A. Shapiro, Wei Cai, Martin Z. Bazant, Andrew M. Minor and William C. Chueh

Constitutive laws underlie most physical processes in nature. However, learning such equations in heterogeneous solids (for example, due to phase separation) is challenging. One such relationship is between composition and eigenstrain, which governs the chemo-mechanical expansion in solids. Here we developed a generalizable, physically constrained image-learning framework to algorithmically learn the chemo-mechanical constitutive law at the nanoscale from correlative four-dimensional scanning transmission electron microscopy and X-ray spectro-ptychography images. We demonstrated this approach on Li$_2$FePO$_4$, a technologically relevant battery positive electrode material. We uncovered the functional form of the composition-eigenstrain relation in this two-phase binary solid across the entire composition range (0 ≤ X ≤ 1), including inside the thermodynamically unstable miscibility gap. The learned relation directly validates Vegard’s law of linear response at the nanoscale. Our physics-constrained data-driven approach directly visualizes the residual strain field (by removing the compositional and coherency strain), which is otherwise impossible to quantify. Heterogeneities in the residual strain arise from misfit dislocations and were independently verified by X-ray diffraction line profile analysis. Our work provides the means to simultaneously quantify chemical expansion, coherency strain and dislocations in battery electrodes, which has implications on rate capabilities and lifetime. Broadly, this work also highlights the potential of integrating correlative microscopy and image learning for extracting material properties and physics.
and contract inside the miscibility gap? To quantify the Li composition and lattice strain in thick-particle specimens, we employed X-ray spectro-ptychography and four-dimensional (4D) scanning transmission electron microscopy (STEM), respectively. Using an image-learning framework employing physical constraint and regularization, we uncovered a mostly linear Li composition–eigenstrain relation (that is, a constant chemical expansion coefficient) in the two-phase binary system across the entire composition range, experimentally validating Vegard's law at the nanoscale. Benchmarked against the non-physically-constrained direct regression results, our image-learning approach reduced the model error by 19%. Importantly, through our framework, we also quantified nanoscale heterogeneities in the residual strain field (that is, those beyond the compositional eigenstrain and coherency elastic strain), which we attributed to plastic deformation through dislocation density analysis. This result was verified independently through X-ray diffraction line profile analysis. These findings are foundational to improving the capacity retention and rate capabilities of phase-transforming battery electrodes, and the method is generalizable to most crystalline materials. Our approach integrates microscopy, materials science and image learning, highlighting the benefits of accurately extracting physical laws from scientific imaging data.

The pipeline for inverse image learning from correlative images is shown in Fig. 1. The procedure consists of three main steps: (1) correlative microscopy, (2) image registration and (3) PDE-constrained optimization. Our objective is to learn the Li composition–eigenstrain relation, \( f(X_i) \), in LiFePO\(_4\) for all compositions (0 \( \leq X \leq 1 \)). Therefore, nanoscale measurement of the composition and strain, particularly at the phase boundaries, is necessary. We employed correlative 4D-STEM and X-ray spectro-ptychography to probe the local lattice constant and Li composition in ten platelet particles (2 \( \times 4 \)\( \mu \)m wide and \( \sim 300 \) nm thick) across 54,508 experimental image pixels. Briefly, 4D-STEM acquires two-dimensional (2D) convergent-beam electron diffraction patterns at every pixel of a 2D STEM raster scan; X-ray spectro-ptychography employs a phase retrieval algorithm to reconstruct the real image as a function of X-ray energy using coherent diffraction patterns whose fields of illumination are overlapped on the sample. The spatial resolution for 4D-STEM (National Center for Electron Microscopy TitanX) reaches 1 nm (refs. 21,41), while X-ray ptychography (Advanced Light Source beamline 7.0.1.2 (COSMIC)) achieves sub-10 nm (ref. 20). We note that STEM electron energy loss spectroscopy, a commonly used approach, is not possible here because of the specimen thickness (<100 nm is generally required), as is often the case for technologically relevant materials such as those for batteries and so on. To ensure the formation of phase-separation boundaries in individual platelet particles, we controlled the Li composition by chemical delithiation rather than by electrochemical cycling to avoid interparticle ‘mosaic’ phase separation (Methods and Supplementary Figs. 1 and 2 for details and general characterization).

For 4D-STEM, taking the unit cell of LiFePO\(_4\) as our unstrained reference, we extracted the lattice parameters \( a \) and \( c \), shear strain \( \gamma \), and rotation angle \( \theta \) from the nanoscale diffraction patterns at each real-space position (Fig. 1, step 1a). The zone axis is along the crystallographic \( b \) axis. The obtained lattice information was then converted into normal strains along the \( a \) and \( c \) axes. The details of the process are in the Methods and Supplementary Fig. 3. For X-ray spectro-ptychography, as shown in Fig. 1, step 1b, the local Li composition \( X_i \) was inferred from the nanoscale X-ray absorption spectra at the Fe L\(_2\) edge (Methods and Supplementary Fig. 4) by assuming local electroneutrality. We acknowledge that the electroneutrality will be violated near interfaces and dislocations. Nonetheless, the very short Debye screening length (<0.1 nm) in LiFePO\(_4\) likely means that such non-electroneutral domains are below our imaging resolution.
In the second step, we align the images by maximizing the correlation between the lattice parameters and Li composition (details in Methods). The aligned image stack (Fig. 1, step 2) contains both compositional and crystallographic features, namely \( \{ X_{ab}, a, c, \gamma, \theta \} \). The constitutive law governing the chemo-mechanics is implicitly embedded in the pixels along the feature space dimension. Finally, in the third step, we learn \( f \) while obeying the stress equilibrium condition:

\[
\mathcal{F} := \nabla \cdot \sigma = 0 \tag{1}
\]

where the left-hand side is the divergence of the stress tensor (\( \sigma \)). In other words, this inverse image-learning problem is a PDE-constrained optimization problem, as illustrated in Fig. 1, step 3.

Figure 2a shows the aligned Li composition and lattice parameter maps of a typical phase-separated \( \text{Li}_x\text{FePO}_4 \) particle. Our technique provides correlational measurement of the composition and lattice constant across phase boundaries. The characteristic widths match within error by phychography (123 ± 39 nm; Fig. 2b and Supplementary Fig. 5) and 4D-STEM (132 ± 41 nm; Fig. 2c and Supplementary Fig. 5) imaging, consistent with some previous literature. While others have reported sharp interfaces (≈10 nm in width)\(^4\), we argue that a sharp phase boundary is unlikely in our case as it would otherwise suggest an energetically unfavourable, >20 degree tilting angle relative to the zone axis\(^4\). Furthermore, the phase-field model sensitivity on the interface width is explored in Supplementary Fig. 6. Before performing inverse image learning of chemo-mechanics, we first carried out a standard data-driven analysis: pixel-wise lattice constant versus Li composition correlation is plotted across ten particles (Fig. 2d–i). We identified the \( \text{Li}_x\text{FePO}_4 \) particles into three categories based on their particle-averaged Li composition: 0 ≤ \( X \) < 0.15 (FP; Fig. 2d), 0.15 < \( X \) < 0.85 (LFP; Fig. 2e) and 0.85 ≤ \( X \) ≤ 1 (LFP; Fig. 2f). In LFP and FP, no phase boundaries were observed, and the mean lattice parameters depend weakly on Li composition. For LFP, while the mean lattice parameters near the end-member compositions were consistent with those of LFP and FP, there were two major differences: (1) the mean lattice parameter changes as a function of composition and (2) the variance of the lattice parameter inside the miscibility gap (≈16% of all pixels, mostly coming from phase boundaries; Supplementary Fig. 5) given a fixed composition was larger than that of LFP and FP.

As mentioned earlier, rigorously distilling the Li composition–eigenstrain relation from the correlated data requires an accounting of various strains under the constraint of stress equilibrium. Specifically, the experimentally observed non-uniform lattice strain arises from three sources: composition-dependent eigenstrain, coherency strain and dislocations\(^4\). We began by first neglecting the dislocation strain in our forward model; we term this the coherency strain model M1, consistent with existing literature\(^{1,39}\). The interpretation of the model error is in Supplementary Note 5. Validity of this assumption will be examined through residual strain analysis later. The remaining two strains sum to the total strain \( \varepsilon \) measured by 4D-STEM; stress is thus expressed as the inner product of stiffness \( C \) (known) and elastic strain: \( \sigma = C : (\varepsilon - f(X_{ab})) \), constrained by the stress equilibrium PDE (labelled as \( \mathcal{F} \)). For discretization during inversion, we directly computed the 2D displacement field \( d \) from \( \{ a, c, \gamma, \theta \} \) (Supplementary Note 1). Consequently, the inverse image-learning problem is: given \( d \) and \( X_{ab} \), what is the composition-dependent eigenstrain relation \( f \) under constraint \( \mathcal{F} \)?

To find \( f \), we parameterized the relation in the following form:

\[
f_i = \sum_{n=1}^{N} a_n L_n (X_{ab}), \ i = 1, 2 \tag{2}
\]

where \( i = 1, 2 \) represents the strain in the \( a \) and \( c \) directions, respectively; \( L_n \) are the Legendre polynomials defined over \( 0 \leq X_{ab} \leq 1 \); and \( a_n \) are the regression coefficients. To the first order, equation (2) gives Vegard’s Law, commonly adopted in alloys\(^7\). Regularization was implemented by fine-tuning the cut-off number \( N \), promoting the sparsity of the fitting parameters to obtain simple physics (details in Supplementary Note 1). Our optimization objective was therefore to minimize the difference \( \| d - \hat{d} \|_M \) between the experimental displacement \( d \) and model prediction based on the PDE constraint \( \mathcal{F} \):

\[
\min \left\{ d, \hat{d} \right\} := \| d - \hat{d} \|_M^2, \text{ subject to } \mathcal{F}(d, f) = 0 \tag{3}
\]

where \( M \) is the difference measure and taken as the Euclidean \( L^2 \) norm. The explicit expressions and derivations are provided in Supplementary Note 1. For benchmarking, we also fitted \( f \) without considering elastic strain or stress equilibrium (hereinafter, direct regression model M0).

The training and test results for model M1 are shown in Supplementary Fig. 7d–i (details in Supplementary Note 1). We found that \( N = 2 \) best avoids systematic overfit. Figure 2g shows the recovered compositional eigenstrain relation for the \( a \) and \( c \) directions, with its 95% point-wise confidence band in the shaded regions. This result indicates that the eigenstrain varies almost linearly with composition, providing a direct experimental validation of Vegard’s law at the nanoscale. By contrast, the benchmark (model M0, direct regression without stress equilibrium constraint, same regularization with four parameters) yielded a more nonlinear compositional eigenstrain behaviour, as shown by the dashed lines in Fig. 2g, which is similar to a previous report on nanosized \( \text{Li}_x\text{FePO}_4 \) (ref. 18) (derived from X-ray diffraction measurements without spatial resolution). The difference in the compositional eigenstrain relation between models M0 and M1 is particularly acute in the
chemical expansion coefficient (that is, derivative of eigenstrain with respect to Li composition), averaging ~28% root mean square difference across the full composition range as shown in Fig. 2h. We note that the chemical expansion coefficient is essential for constructing the chemical potential in phase-field theories \(^{13,39}\) (derivation in Supplementary Note 2). Physically, the difference between the two models is the coherency (elastic) strain, which model M0 neglects. As we detail later, physics-constrained inverse image learning produces less error than the direct regression model despite having fewer parameters. Additionally, we highlight that the compositional eigenstrain relationship can be identified and remains consistent from a single image stack, as increasing the number of image stacks shrinks the confidence band only slightly (Supplementary Fig. 8; details in Supplementary Note 1). Our approach highlights the importance of physics-informed image inversion rather than a pure data-driven approach, the latter of which does not guarantee consistency with solid mechanics.

Having extracted the Li composition–eigenstrain relation, we generate additional chemo-mechanical insights from the residual strain field. As a case study, we focus on a single phase-separated particle with an average Li composition of \( \bar{X} = 0.51 \). The Li composition map and the total strain field (measured by 4D-STEM) are presented in Fig. 3a. Given the experimental Li composition and \( f \), coherency strain is computed from 2D phase-field
Fig. 3 | Chemo-mechanical insights of Li$_x$FePO$_4$. a, Experimental observation of Li composition and total (lattice) strain field $\varepsilon$ (measured by 4D-STEM, unitless) of Li$_{0.51}$FePO$_4$. Well-defined phase boundaries are formed inside chemo-mechanically equilibrated Li$_x$FePO$_4$, with an orientation close to the [101] direction. Subscripts $aa$ and $cc$ correspond to normal strain in the $a$ and $c$ directions, and $ac$ represents $ac$-shear strain. Arrows represent the average crystallographic axis. b, The residual strain field, defined as the total strain minus the compositional eigenstrain and coherency (elastic) strain. Coherency strain is computed by 2D phase-field simulations. The residual strain field is highly non-uniform and displays local hot spots in residual $\varepsilon_{aa}$, $\varepsilon_{cc}$ and $\varepsilon_{ac}$. These hot spots are located around the phase boundaries and inside the phase-separated regions, indicating the existence of other types of strains, for example dislocations. c, Simulated dislocation density of type D [001][100] and its residual strain field. The particle-averaged dislocation density is $\sim$282 $\mu$m$^{-2}$, consistent with the independent X-ray line profile analysis. The dislocations are not necessarily located at phase boundaries (red dashed line), as interfaces move during delithiation. Many of the local hot spots in the residual strain field are recovered, except for regions where 4D-STEM measurement has higher uncertainty, shown in Supplementary Fig. 13. d, Residual strain incompatibility as a function of particle-averaged Li composition. Effects of the heterogeneities can be quantified through the residual strain incompatibility—that is, the root mean square residual of the compatibility condition at each pixel. The dashed line is a guide to the eye. Visualization of the residual strain field for all particles is in Supplementary Fig. 10. e, Model error—that is, the mean Frobenius norm of residual strain—from the three models: direct regression (M0, baseline), coherency strain (M1) and dislocation (M2). For a fair comparison, all model errors were converted into strain. M1 has a 19% reduction in model error from M0, while M2 has a 43% reduction compared with M0. Scale bar, 1 $\mu$m.
models with experimental conditions (Supplementary Fig. 9e; details in Supplementary Note 2). Next, we visualize the experimental residual strain field, defined as the total strain minus the compositional eigenstrain and coherency strain (Supplementary Note 3). Figure 3b shows significant local heterogeneities in the residual strain, which are consistently observed throughout L_{0.5}FP particles (Supplementary Fig. 10). Such local hot spots impact strain compatibility (details in Supplementary Note 3).

The root mean square residual strain incompatibility versus particle-averaged Li composition reaches a maximum at \( X \approx 0.5 \) (Fig. 3d). These strain hot spots may be due to morphological defects; the particles studied are not uniformly thick and contain voids, as observed from X-ray tomography (Supplementary Fig. 11). To assess this hypothesis, we employed a three-dimensional (3D) phase-field simulation on similarly sized and shaped particles with internal pores (Supplementary Fig. 12). However, no local hot spots in the residual strain were observed. Having ruled out pore effects, the residual strain heterogeneities likely arise from misfit dislocations.

Indeed, simulation based on misfit dislocations (Supplementary Note 4) among potential dislocation systems generated residual strain maps similar to the experimental observations (Fig. 3c), except for regions where 4D-STEM measurement has a higher uncertainty (Supplementary Fig. 13). Motivated by these results, we constructed a dislocation model (M2) that includes compositional eigenstrain (same parameterization as M1), coherency strain and dislocation effects (parameterized by the dislocation density of different dislocation types), detailed in Supplementary Note 4. Supplementary Fig. 14 shows that the dislocation model error was minimized when the Burgers vector was along the crystallographic \( \langle 101 \rangle \) direction, with an average density of \( \approx 282 \mu \text{m}^{-2} \) (Fig. 3c). We note that such dislocations are not necessarily localized at the phase boundaries as the boundaries move during delithiation. We highlight that this dislocation strain field is otherwise impossible to quantify without accounting for compositional and coherency strains. Additionally, we note that while transmission electron microscopy (TEM) is the preferred method to visualize dislocations, the large specimen thickness (\( \approx 300 \) nm) made imaging impossible due to dynamic scattering. Our approach therefore enables non-destructive imaging of dislocations in thick specimens at the nanoscale.

We assess the effectiveness of the physical constraint for inverse image learning through residual error analysis. Figure 3e compares the model errors of the direct regression model (M0), coherency strain model (M1) and dislocation model (M2). Benchmarked against M0 (baseline), M1 reduces the model error by 19%, and M2 reduces the model error by an additional 24%. From a data science perspective, the principle of parsimony favours M1 over M0 because of its increase in model accuracy yet decrease in the number of parameters. More broadly, this result emphasizes the benefits of having appropriate physical constraints for inverse image learning. On the other hand, independent validation of the M2 model is necessary as the local dislocation density is a spatially dependent variable that scales quadratically with the image size.

We turned to X-ray powder diffraction to independently verify the dislocation density. Specifically, we employed a variance-based line profile analysis to evaluate the dislocation densities and types. As shown in Fig. 4, the dislocation-induced broadening was the highest for FP, intermediate for L_{0.5}FP (powder with an average Li composition of 0.5) and smallest for pristine LFP (which has never seen the formation of phase boundaries). Furthermore, because each dislocation carries a unique angle-dependent broadening signature, we used non-negative least squares minimization to identify the major dislocation systems. Table 1 shows the most likely dislocation combinations for LFP, L_{0.5}FP and FP. Relevant analysis is presented in Supplementary Note 6. The total dislocation density increases with the delithiation extent. Specifically, the dislocation system \( \langle 101 \rangle \) in short (representing dislocations with \( [001] \) Burgers vector and \( (100) \) slip plane) with an estimated density of \( 306 \pm 97 \mu \text{m}^{-2} \), is consistent with the dislocation density determined from model M2. Other candidates (whose line directions are not aligned with \( [010] \)) do not substantially alter the local strain field in the crystallographic \( ac \) plane measured through 4D-STEM. The result is also consistent with the fact that the formation of misfit dislocations with a smaller Burgers vector magnitude is thermodynamically more favourable. Interestingly, after complete delithiation, the dislocation contributing to the \( ac \)-plane strain disappears, consistent with residual strain analysis (Fig. 3d). Investigation of dislocation dynamics is underway. Finally, the estimated dislocation density is of a similar order of magnitude to that of other battery positive electrodes observed during/after cycling.

In summary, we presented an inverse image-learning framework that combines state-of-the-art high-resolution X-ray and electron microscopy with PDE-constrained optimization. The functional form of the composition–eigenstrain relation across the full Li composition range was quantified in the phase-separating system Li_{1-x}FePO_4. Benchmarked against the constraint-free baseline model, our approach reduced the model error by 19%. Removing the compositional and coherency strain also revealed the residual strain heterogeneities in phase-separated particles. Local heterogeneities are likely due to edge dislocations of \( [001] \) (100), which further reduced the model error by an additional 24%. Previous studies have reported a correlation between dislocations and battery rate...
Table 1 | Identification of dislocation systems

| n   | Label | b        | l        | Type   | LFP | L0.5FP | FP  |
|-----|-------|----------|----------|--------|-----|--------|-----|
|     |       |          |          |        | 1,257(80) | 2,147(173) | 4,619(351) |
| (100)| A     | [010]    | [001]    | Edge   | 87  | 91     | 85  |
|     | B     | [010]    | [011]    | Mixed  | 590(183) | 1,298(183) |
|     | C     | [010]    | [021]    | Mixed  | 192(39)  | 306(97)  |
|     | D     | [010]    | [010]    | Edge   | 247(16)  | 735(106)  | 1,382(146) |
|     | E     | ½[011]   | [111]    | Mixed  | 692(67)  | 457(149)  |
|     | F     | ½[011]   | [010]    | Mixed  | 45(15)   | 556(82)   | 1,939(261) |
| (010)| G     | [001]    | [100]    | Edge   | 264(14)  | 247(16)  | 735(106)  |
|     | H     | ½[011]   | [101]    | Mixed  | 692(67)  | 457(149)  |
|     | I     | [010]    | [110]    | Mixed  | 45(15)   | 556(82)   | 1,939(261) |
|     | J     | [010]    | [110]    | Mixed  | 247(16)  | 735(106)  | 1,382(146) |
|     | K     | [010]    | [120]    | Mixed  | 692(67)  | 457(149)  |
|     | L     | ½[110]   | [110]    | Mixed  | 45(15)   | 556(82)   | 1,939(261) |
|     | M     | ½[110]   | [010]    | Mixed  | 247(16)  | 735(106)  | 1,382(146) |
| (011)| N     | ½[011]   | [100]    | Edge   | 264(14)  | 247(16)  | 735(106)  |
| (110)| O     | ½[110]   | [001]    | Edge   | 692(67)  | 457(149)  |

Labelled systems are considered for regression; n is the index plane normal, b is the Burgers vector and l is the sensing vector. All candidates are either edge or mixed dislocations. The value in the parenthesis represents the standard deviation. Total dislocation densities increase with the delithiation extent. In the dislocation systems with non-negative values, only system D contributes to the residual ac-plane strain field measurable by 4D-STEM.

capabilities as well as lifetime28,29; our findings provide the means and motivation for attaining a more fundamental understanding of dislocations inside battery electrodes. Broadly speaking, our approach to infer physics through image inversion is highly applicable to other systems, particularly those that traditionally face thermodynamic or characterization limitations15. We anticipate that the same approach can be adapted for dynamic systems, where the laws governing the reaction kinetics and transport can be learned22,29. The proposed method demonstrates the potential of merging correlative microscopy with physics-constrained image learning for scientific discovery.

Online content
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Methods
Synthesis. LiFePO₄ platelets were synthesized using a solvothermal method modified from previous work. All the precursors were purchased from Sigma-Aldrich. In detail, 6 ml of 1 M H₂PO₄ was mixed with 24 ml of polyethylene glycol 400. Then, 18 ml of 1 M LiOH (aq) was added to precipitate LiOH. The mixture was constantly bubbled with dry N₂ at a flow rate of ~50 ml/min for ~16 h for deoxygenation. Next, 12 ml of deoxygenated H₂O was added via a Schlenk line to FeSO₄·7H₂O powder, which was preheated under vacuum. The FeSO₄ solution was then injected into the LiPO₄ suspension without oxygen exposure, and the entire mixture was transferred to a 100 ml Teflon-lined autoclave. The autoclave was heated to 140 °C for 1 h and then to 210 °C for 17 h. Note that this synthesis method produces smooth, flat and well-faceted platelet particles but not void-free particles. The sample from this batched synthesis is referred to as BA1. The sample was annealed under Ar gas at 720 °C for 5 h to eliminate anti-site defects. Note that the sample for correlative imaging was not carbon coated.

Delithiation of LiFePO₄. To avoid interparticle phase separation, also known as a mosaic pattern, we chemically delithiated the pristine LiFePO₄ particles using a redox titration platform. This process ensured the formation of phase boundaries after phase separation and eliminated kinetic heterogeneities resulting from the carbon coating during electrochemical delithiation. Dilute suspension (1 mg ml⁻¹) of LiFePO₄, Li₀.₅FePO₄ (L₀.₅FP) and FePO₄ (FP). To minimize the titration rate was optimized to 5 ml h⁻¹ and the suspension was continuously stirred at 500 r.p.m.

Electrochemical characterization. Given the relevance of the particles for battery applications, we electrochemically tested the materials compared to commercial LFP powders. Specifically, pristine LiFePO₄ was carbon coated by mixing with sucrose (LFP/sucrose = 5:1 w/w) and annealing under Ar gas at 720 °C for 5 h (refs. 22, 45); cast as an electrode sheet; and then assembled into 2032-type lithium half cell. The tests confirmed the industrial relevance of the materials studied, and atomic force microscopy analyses of the pristine and chemically delithiated morphological characterization, scanning electron microscopy, X-ray diffraction for structural and morphological characterization.

X-ray microscopy. Scanning transmission X-ray microscopy measurements were performed at beamlines 11.0.2 and 7.0.1.2 (COSMIC) using a zone plate with an outer zone width of 45 nm. Images at different X-ray energies were aligned using the ETEC alignment algorithm. The Fe L2 edge was used to determine the local state of charge. LiFePO₄ and FePO₄ were selected as reference samples, with a full range energy stack taken at a step size of 0.2 eV from 696 eV to 740 eV. The local composition was thus determined based on the absorption at five selected energies (700 eV, 706.2 eV, 708.6 eV, 711.2 eV and 713.4 eV, covering one pre-edge, two rising edges and two falling edges) using a non-negative least squares optimization algorithm. We deliberately avoided on-edge measurement because of the ill-measured photosensitivity from thick samples. Ptychography measurements were performed at beamline 7.0.1.2 (COSMIC) at the Advanced Light Source and were taken in double-exposure mode. Ptychographic reconstruction was performed using standard methods available in the SHARP-CAMERA software package with parallel computation (http://camera.lbl.gov/). The spatial resolution was calculated by Fourier ring correlation to be 10 nm (half-bit threshold) at 710 eV (Supplementary Fig. 4b). The same particle was imaged in scanning transmission X-ray microscopy before and after the X-ray ptychography measurement, and no major changes in local composition were observed, suggesting low X-ray damage to the composition.

Image registration. The 4D-STEM and X-ray spectro-ptychography were used to probe the local lattice and chemistry of the sample and generate a high-dimensional dataset from each of the measurements. To understand the correlation between the structure and chemistry, the two sets of images were then registered through an affine transformation that maximizes the correlation scoring function between the electron images (from 4D-STEM) to X-ray images (from X-ray spectro-ptychography) using custom MATLAB code.

Structural and morphological characterization. For structural and morphological characterization, scanning electron microscopy, X-ray diffraction and atomic force microscopy analyses of the pristine and chemically delithiated samples were performed. Scanning electron microscopy was performed using a Sirion (FEI) machine at the Stanford Nano Shared Facility. A primary diamond-shaped particle structure with feature dimensions of 4 × 0.3 × 2 mm² (in the cryo-TEM, a and c directions) was observed for the BA1 particles. No notable morphological change was observed after chemical delithiation. The BA1 particles contained morphological defects, which were later characterized using X-ray tomography. X-ray diffraction was first performed on a Bruker D8 at Stanford for structural characterization and at beamline 2-1 at the Stanford Synchrotron Radiation Lightsource at 17.3 keV using energy. A Lab, standard reference material was used for calibration of the set-up and instrumental broadening. The capillaries were 0.5 mm special glass capillaries (Charles Supper) and were loaded inside an Ar-filled glove box. The samples were rotated continuously throughout the measurement to avoid preferential orientation effects. The beam was 0.5 mm in width and 1 mm in height. Raw data were recorded using a Peltier-cold stage, 700 μm distance from the capillary sample. For atomic force microscopy, the LiFePO₄, FePO₄ platelet was dispersed with isopropyl alcohol onto mica and imaged using an Asylum Cypher ES scanning probe microscope. Image processing including flattening was performed using the built-in Asylum software package based on Igor Pro.

Sample dispersion for correlative X-ray microscopy and 4D-STEM imaging. Pristine LiFePO₄, Li₀.₅FePO₄ and FePO₄ platelets were dispersed with deionized water and sonicated for 2 h under an ice bath. The top layer was extracted, followed by the same procedure as the previous step until a clean, uniform particle suspension was formed. The particles were then dispersed onto a TEM grid (Ted Pella, 200 mesh with reference index). The TEM grid was loaded into a TEM instrument (TitanX) at the National Center for Electron Microscopy and then at the COSMIC beamline at the Advanced Light Source for correlative imaging.

4D-STEM. The 4D-STEM was performed at the National Center for Electron Microscopy using a TitanX, operated at an accelerating voltage of 300 kV with a convergence semi-angle of 0.48 mrad using a 40 μm condenser (C2) and a camera length of 600 mm. The probe size was 2.2–2.5 nm with a step size of 49.5 nm or 16.6 nm. During the imaging, a condensed electron beam was raster scanned across the sample, with a diffraction pattern acquired at each scan position. Local information on the lattice, including the strain and rotation, was obtained using py4DSTEM, an open-source python package available at https://github.com/py4DSTEM/py4DSTEM. 

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Code availability
The codes used for image registration and image inversion can be accessed at https://github.com/dhithean/correlative-image-learning. Additional code is available from the corresponding authors upon reasonable request.
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Author contributions
H.D.D., N.J., W.C.C. and A.M.M. conceived the experiments. H.D.D., N.J. and E.G.L. performed the synthesis and materials characterization. H.D.D. and N.J. performed the STXM and ptychography experiments. H.D.D. performed the STXM and X-ray spectro-ptychography data analysis. Y.-S.Y. and D.A.S. contributed to the scanning transmission X-ray microscopy and ptychography experiments. L.H. performed the 4D-STEM experiments. C.O. performed the image registration. L.H. and B.H.S. performed the 4D-STEM analysis. H.D.D., H.Z. and M.Z.B. developed and performed the inverse image-learning optimization. R.Y. and J.L. contributed to the early algorithmic exploration of PDE-constrained optimization. H.D.D. and W.C. performed the 2D phase-field simulation and dislocation density optimization. D.F. performed the 3D phase-field simulation. H.D.D. and W.C. and A.B. performed the X-ray line profile analysis. Y.-S.Y. analysed the ptycho-tomography data. H.D.D. prepared the manuscript. All authors contributed to the discussion of the results and writing of the manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Andrew M. Minor or William C. Chueh.
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