Localized concentration reversal of lithium during intercalation into nanoparticles

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Nanoparticulate electrodes, such as LiFePO4, have unique advantages over their microparticulate counterparts for the applications in Li-ion batteries because of the shortened diffusion path and access to nonequilibrium routes for fast Li incorporation, thus radically boosting power density of the electrodes. However, how Li intercalation occurs locally in a single nanoparticle of such materials remains unresolved because real-time observation at such a fine scale is still lacking. We report visualization of local Li intercalation via solid-solution transformation in individual LiFePO4 nanoparticles, enabled by probing sub-angstrom changes in the lattice spacing in situ. The real-time observation reveals inhomogeneous intercalation, accompanied with an unexpected reversal of Li concentration at the nanometer scale. The origin of the reversal phenomenon is elucidated through phase-field simulations, and it is attributed to the presence of structurally different regions that have distinct chemical potential functions. The findings from this study provide a new perspective on the local intercalation dynamics in battery electrodes.

Li-ion batteries (LIBs) are preferred energy storage devices for portable electronics and are becoming important power sources for electric vehicles and grid-scale storage (1). In commercial battery electrodes, such as layered oxides (LiCoO2, LiCo0.13Ni0.13Mn0.74O2) (2, 3), spinel (LiMn2O4) (4), and olivine [LiFePO4 (LFP)] (5), electrochemical reactions take place through an intercalation process, during which Li ions are inserted into interstitial sites of the host without causing significant structural changes in the electrodes (2, 6–10). Li intercalation can occur either through a two-phase transformation path (in which the fully lithiated phase nucleates and grows) or through a single-phase solid-solution transformation path (in which no phase boundaries form). Owing to the recent development of in situ probing techniques, significant progress has been made in understanding of intercalation dynamics and related phenomena in LIBs. Notably, direct observation of such processes has been hindered by the lack of spatial resolution for ex situ studies revealed that in many of the material systems, especially nanoparticulate ones, fast Li incorporation may occur via nonequilibrium routes, radically boosting power density of the electrodes (6, 11–17).

Nanoparticulate electrodes, such as LFP, have unique advantages over their microparticulate counterparts for the applications in LIBs because of the shortened diffusion path and have been extensively investigated over the past decade (18). LFP is an important commercial cathode material known for its superior safety and cycling stability. However, the origin of high-rate capability found in LFP has been a subject of debate because it is in conflict with the common belief of a sluggish two-phase transformation process in this material (19). Recent atomistic calculations predicted a nonequilibrium intercalation process that occurs via a single-phase solid-solution transformation during fast lithiation of nanosized LFP because of a low energy barrier for the transformation between LFP and FePO4 (FP) (20). This nonequilibrium process provided the first explanation for the high-rate capability (11, 15, 20–24). The latest studies also showed that, even at low-to-moderate cycling rates, solid-solution states might still persist within broad, diffuse interfaces between LFP and FP phases (24–26). Moreover, the solid-solution transformation mechanism can lead to new electrochemical behaviors, such as Li redistribution between neighboring particles in multiparticle systems (19, 27–30). Similarly, Li redistribution may also occur in other electrode materials (31).

Compared to the significant progress in theory and modeling, experimental studies on electrochemical reactions in nanoparticulate LFP have lagged far behind, and no concrete evidence of solid-solution transformation was found until very recently, through fast in situ x-ray diffraction (XRD) measurements (11, 23). Another study via in situ scanning transmission x-ray microscopy (STXM) provided new evidence of solid-solution phase transformation even in micrometer-sized LFP particles, which identified ~100-nm-scale heterogeneity within particles (15). Yet, x-ray–based in situ techniques have spatial resolution for exploring local Li intercalation and the associated structural changes within individual nanoparticles (19, 27–30). High-resolution transmission electron microscopy (HRTEM) is capable of exceptional spatial resolution, and it has recently been developed for in situ tracking of the phase evolution, providing otherwise inaccessible details, such as the formation of misfit dislocations and solid-solution zones between FP and LFP during the two-phase transformation (26, 32). However, without the formation of distinctive phase boundaries during a monophasic solid-solution transformation in LiFePO4, the subtle change in lattice spacing, at the sub-angstrom scale, cannot be directly resolved by in situ HRTEM (26).

Here, we report advancement in situ techniques enabling real-time tracking of Li intercalation in a single nanoparticle through electron diffraction (ED) and locally within nanosized domains via...
HRTEM imaging coupled with geometric phase analysis (GPA). Modification was made to the algorithm of GPA, making it suitable for in situ detection of sub-angstrom changes of lattice spacing (33). More specifically, a new function was integrated into GPA for processing time- and position-resolved lattice images, allowing for direct correlation of local displacement with the concentration of intercalated Li within a single solid-solution phase. Therefore, this method enables real-time visualization of the evolution of local Li concentration within a single nanoparticle, which is not achievable via ex situ measurements (34). Local Li intercalation dynamics in FP nanocrystals was visualized via this new approach, which revealed an inhomogeneous solid-solution transformation process within a single nanoparticle, accompanied with a surprising reversal of local Li concentration at the nanometer scale. Phase-field simulations were performed to elucidate the thermodynamic origin of the reversal phenomenon, which indicated that the presence of spatially varying chemical potential functions within the nanoparticle leads to such concentration reversal. The findings from this study provide new insights into local dynamics of electrochemically driven phase transformations within individual particles in intercalation-type battery electrodes.

RESULTS

Technique development for in situ tracking of local Li intercalation

Figure 1 illustrates the experimental setup for tracking local Li intercalation within individual FP nanoparticles. For this study, plate-shaped single-crystalline nanoparticles (shown in fig. S1A) were synthesized through a solvothermal procedure (35) and coated with a thin carbon layer [characterized using electron energy-loss spectroscopy (EELS) mapping; Fig. 1A]. A TEM grid–based composite electrode was made of carbon-coated FP nanoparticles loaded on the carbon film (Fig. 1B), and during the measurements, could be connected to the Li-coated tip to activate electrochemical reactions under potentiostatic conditions (see details in Materials and Methods) (17). As shown in Fig. 1C, those TEM grid–based electrodes exhibited high-rate capability, comparable to that in normal composite electrodes (fig. S2) (35). FP nanoparticles were well dispersed on the TEM grids, and those isolated individuals were selected for in situ ED measurements with the electron beam along a certain zone axis (that is, b axis; parallel to the fast Li diffusion channel), as illustrated in Fig. 1B. In addition, this configuration allows tracking of local Li intercalation within a single FP particle, through high-resolution lattice imaging coupled with GPA analysis. With a modified GPA algorithm (see Materials and Methods), the lattice image taken from a selected area in the pristine sample (with lattice spacing $a_{\text{ref}}$) is used as the reference, and correspondingly, the evolution of lattice spacing as a function of time, $D_a(r, t)$, relative to that of the pristine sample can be extracted from the subsequent lattice images

$$\Delta a(r, t) = -a(r)a_{\text{ref}}\Delta g$$

where $a(r)$ is the lattice spacing in the subsequent images taken from the selected area and $\Delta g$ is the deviation from the ideal reciprocal lattice vector. Because of the strong correlation between lattice spacing and Li concentration in Li$_x$FePO$_4$ (11, 36), the two-dimensional (2D) lattice spacing maps generated as a function of time are highly sensitive to the

Fig. 1. Experimental setup for in situ tracking of local Li intercalation within a single-crystalline nanoparticle. (A) Chemical image of the representative FP nanoparticles for in situ measurements (mapped via EELS; Fe: red, C: green). The particles are plate-like single crystals, thin in the [010] crystalline axis (inset); scale bar, 100 nm. (B) Schematic illustration of the in situ electrochemical cell containing a half-TEM grid loaded with FP nanoparticles, which enables in situ ED and HRTEM measurements at the single or subparticle level. The HRTEM imaging coupled with GPA (using a new algorithm as given in Materials and Methods) generates the spatial distribution of Li concentration in local areas of a single nanoparticle. STM, scanning tunneling microscope. (C) Demonstration of the high-rate capability of FP nanoparticles in the TEM grid–based electrodes. The voltage profiles are similar to those obtained from standard coin cells (fig. S2).
spatial and temporal variations of Li concentration and thus serve as a probe for the intercalation processes in local areas within a single-crystalline nanoparticle.

**Nonequilibrium intercalation via solid-solution transformation**

In situ ED measurements were conducted on a single FP nanoparticle during lithiation to determine the pathway of phase transformation (that is, single- or two-phase mechanisms) at the single-particle level. Time-resolved ED patterns were recorded at a frequency of two patterns per second from a selected FP nanoparticle (approximately 35 nm wide and 58 nm long; fig. S3) upon lithiation at a rate equivalent to ~18 C, where C is the single-particle rate (defined using a similar method in the previous work) (15). The main results are given in Fig. 2 and movie S1, wherein the nanoparticle was tilted to [010] zone axis, allowing the tracking of the changes in the a and c lattice parameters using diffraction spots of {200} and {001}, respectively (Fig. 2A). The initial single (200) spot associated with the FP phase (a = 9.83 Å, c = 4.78 Å) gradually split due to the formation of Li$_x$FePO$_4$ (0 < x < 1) as lithiation proceeded. Figure 2B shows a representative ED pattern recorded after 113 s of lithiation, corresponding to the Li$_x$FePO$_4$ with lattice parameters, a = 10.05 ± 0.01 Å and c = 4.71 ± 0.01 Å. The splitting of the diffraction spot is subtle because of the small lattice change, so the intensity profiles of the diffraction spots were extracted to show the gradual changes in the ED. Figure 2C shows the intensity profiles of the (200) spot as a function of lithiation time. When the lithiation started (at 0 s), the (200) peak became broadened, and with further lithiation, at about 13 s, a new, barely separated peak became visible. The gradual separation, with the peak on the left [corresponding to a shorter distance between (200) to the central spot] continuously shifting to the left, indicates the formation of Li$_x$FePO$_4$ of increasing Li content through a continuous solid-solution transformation (36). At the end of lithiation (at ~203 s), the shift of the (200) peak from that of the initial FP phases corresponds to a lattice expansion of nearly 4.7%, close to the theoretical misfit of 5.0% between LFP and FP (37). The gradual decrease in the lattice parameter c was also observed from the evolution of the (001) diffraction spot (fig. S4). In addition, the reduction of Fe valence state due to lithiation was determined by EELS (via the chemical shift of Fe L-edge spectra; fig. S5). Therefore, our in situ ED measurements unambiguously identified the solid-solution transformation in a single nanoparticle of known size and morphology.

The evolution of the relative change in lattice spacing a versus lithiation time, defined by $e_a = (a_{Li_xFePO_4} - a_{FP})/(a_{FP} - a_{LFP})$, was also extracted from the intensity profiles and plotted in Fig. 2D. The gradual increase of $e_a$ with time during the solid-solution transformation was highly nonlinear. For example, a slow increase of the lattice spacing a was observed in the intermediate stage (between 40 and 150 s), in contrast to an abrupt increase in the initial and final stages. The estimated values of the lattice spacing within the intermediate stage correspond to a Li concentration range of x = 0.3 to 0.6 in Li$_x$FePO$_4$ based on Vegard’s law (22, 36, 38, 39), which is close to the composition between Li$_{0.25}$FePO$_4$ and Li$_{0.65}$FePO$_4$, determined by in situ XRD measurements from agglomerates of nanoparticles (11). However, the nonlinear evolution of composition during the solid-solution transformation was not observed by in situ XRD.

**Fig. 2.** In situ ED measurements indicating a solid-solution transformation in a single Li$_x$FePO$_4$ nanoparticle. Representative ED patterns recorded from a b-oriented FP nanoparticle (shown in fig. S3) at (A) the pristine state and (B) an intermediate state after 113 s of lithiation. The splitting of the (200) and (001) diffraction spots indicates the transformation from FP (marked by black arrows) to Li$_x$FePO$_4$ (red ones). (C) Evolution of intensity profiles of the (200) diffraction spots versus the distance from the center (000). Dots: original data; solid lines: fitted ones by weighted Gaussian and Lorentzian functions. (D) Evolution of relative change of lattice spacing a, defined by $e_a = (a_{Li_xFePO_4} - a_{FP})/(a_{FP} - a_{LFP})$, where the lattice parameter $a_{Li_xFePO_4}$ was measured from the peak positions in the fitted profiles in (C) (being marked with red vertical lines), as a function of the elapsed time (shown by red triangles); the dashed curve is a guide to the eye. The error bars correspond to the standard deviation obtained from four diffraction spots ±(100) and ±(200). a.u. arbitrary unit.
Li concentration reversal within nanosized domains

Following the in situ ED examination of the lattice spacing averaged over an entire nanoparticle, in situ lattice imaging was used to further investigate the local intercalation process on another FP nanoparticle. The main results are given in Fig. 3. All of the lattice images recorded at different lithiated states from an area of about $47 \times 47$ nm$^2$ (as marked by the blue box in Fig. 3A) are given in fig. S6. The lattice spacing is highly homogeneous, as demonstrated by the magnified view of the lattice image (inset in Fig. 3A; for a $10 \times 10$ nm$^2$ area as marked by the red box). Fast Fourier transformation (FFT) patterns were extracted from the lattice images of the selected area to examine the evolution of the lattice spacing using a similar approach as in the in situ ED measurements. The gradual change of the lattice spacing with time (as displayed in fig. S7, A and B) is overall similar to the observations by in situ ED (Fig. 2C and fig. S4), again indicating a solid-solution transformation process, with temporal nonlinearity (that is, a relatively slower increase of lattice spacing $a$ in the intermediate lithiation stage between 40 and 150 s). These results indicate that the FFT analyses of the HRTEM images from a portion of FP nanoparticles captured the solid-solution transformation discovered from in situ ED measurements of an entire nanoparticle. However, by comparing the FFT patterns from different areas (as illustrated in fig. S8), it can be found that the lattice displacement during a monophasic solid-solution lithiation process was significantly different from one area to another. To map the local, lithiation-driven lattice displacement in FP throughout the viewed area, a redesigned GPA method was used to process the in situ HRTEM images (detailed in Materials and Methods). During a single-phase solid-solution transformation, phase boundaries, which would manifest as an abrupt change in local coherent lattice strain, do not form, but rather one single phase of varying Li concentration forms (11, 24). Therefore, Vegard’s law is applied here to convert the local lattice displacement into Li concentration distribution at different lithiation states (Fig. 3, B to I). The evolution of Li concentration shows that the solid-solution transformation proceeded continuously and heterogeneously across the entire area of view, without forming distinctive Li-poor $\text{Li}_x\text{FePO}_4$ ($0 < x < 0.2$) or Li-rich $\text{Li}_{1-x}\text{FePO}_4$ ($0.8 < 1 - x < 1$) phases (40, 41). Instead, only noticeable concentration gradients between neighboring regions with relatively high and low Li concentration appeared during the entire lithiation process (as shown in fig. S9). This observation is significantly different from that in micrometer-sized FP particles, in which the two distinctive phases coexist (32, 42).

Quantitative analysis was also applied to the local Li concentration distribution in Fig. 3 (B to I) by sampling the data over a certain selected area, such as A with a dimension of $3 \times 3$ nm$^2$ (as illustrated in Fig. 3B). The averaged concentration in A is plotted by the red dashed curve in Fig. 3J. Surprisingly, a reversal in Li concentration over time was

![Fig. 3. Visualization of the Li concentration evolution at sub-nanoscale within a single-crystalline Li$_x$FePO$_4$ nanoparticle during lithiation (at a rate of ~18 C). (A) Bright-field image and expanded view of the local lattice image from a single-crystalline FP nanoparticle (about 113 nm in width and 120 nm in length) at the pristine state oriented along [010] (scale bars, 50 and 5 nm, respectively). (B to I) 2D maps of local Li concentration ($x$ in Li$_x$FePO$_4$) at a series of lithiated states for the selected area marked by the blue box in (A), which were derived from the lattice displacement of (100) planes relative to the pristine state (see fig. S6 for HRTEM images and Materials and Methods for the GPA processing). Color scale next to (B) indicates the lattice expansion $\Delta a$ (relative to the lattice spacing $a$ at the pristine state) and corresponding normalized Li concentration $x$. Scale bars, 5 nm. (J) Evolution of the averaged Li concentration ($x$) averaged over selected areas with different sizes [as marked by squares in (B) to (I)].](https://sciadv.sciencemag.org/content/early/2018/02/19/sciadv.201800372087_f3.png)
observed, in which the concentration increased rapidly in the early stage (up to approximately 0.6 by 59 s) and subsequently dropped to about 0.1 (at 121 s). Thereafter, the averaged Li concentration increased again, up to about 0.7 by 200 s. Multiple regions experience such Li concentration reversal within the samples examined, as demonstrated in fig. S9. Here, we note that the calculated composition may include a small error because the effect of lattice relaxation was neglected. However, if the effect of lattice relaxation is taken into account in the analysis, the amplitude of reversal in concentration will be greater. Therefore, the general conclusion is not affected when considering the effect of lattice relaxation. Furthermore, it is clear that the concentration reversal does not originate from concentration fluctuation due to thermal noise because the length scale of the concentration reversal observed in the experiment is much larger than that associated with clustering, dissolution, and nucleation for the LFP phase. The critical radius for forming an LFP nucleus, estimated following the classical nucleation theory used by Malik et al. (20), is ~0.3 nm under an apparent overpotential of 3 V, a condition corresponding to this experiment. Clusters much larger than this size are expected to grow, not dissolve, solely because of thermal fluctuation under the condition. The results thus indicate that a thermodynamic driving force underlying the concentration reversal exists.

A similar approach was applied to extract the averaged Li concentration from areas of additional sizes of data sampling, namely, 10 × 10 nm² and 20 × 20 nm² (labeled by B and C, respectively, in Fig. 3B), also showing a similar phenomenon of Li concentration reversal (Fig. 3J). However, the comparison between the curves shows a strong dependence of the Li concentration reversal on the size of the sampling areas, with an abrupt reduction of the amplitude as the sampling size was increased to 10 × 10 nm² (as in region B). The concentration reversal became negligibly small in region C (of 20 × 20 nm²), and when the sampling size was further increased to the entire area (in the blue box in Fig. 3A), the reversal was no longer observable, indicating that the concentration reversal is a highly localized phenomenon, and may be obscured when the resolution is insufficient. Another striking feature is an opposite concentration undulation in the regions adjacent to each other, for example, in the lower left corner of region B versus that in the upper left corner (fig. S10). Such an anticorrelated concentration undulation between neighboring areas is a manifestation of the intraparticle redistribution of Li. Thus, unless the imaging resolution affords the distinction between these regions with undulated concentration evolution, the concentration reversal phenomenon would not be detectable. In the recent studies of Li intercalation within a single LFP particle using in situ XRD (24) and in situ STXM techniques (15), no reversal but continuous evolution of Li concentration in the intermediates was observed, probably because of the limited spatial resolution (~100 nm or lower), under which the reversal became averaged out.

**DISCUSSION**

The localized Li concentration reversal within nanometer regions of FP nanoparticles (Fig. 3), along with the redistribution of Li (fig. S10), has not been reported in the literature to the best of the authors’ knowledge. This phenomenon resembles the interparticle Li redistribution in a multiparticle system (27–30). In nanoparticulate LFP cathodes, particles lithiate differently because of different surface area-to-volume ratio (28, 29) or particle positions (19). Driven by the difference in chemical potentials between neighboring particles that have lithiated to different states, interparticle Li redistribution occurs and results in a certain degree of concentration reversal of those lithiated particles. Analogous to such interparticle dynamics (19, 28), within a particle, some regions may lithiate faster than their surrounding areas. Hereafter, for convenience, we denote the fast-lithiating regions as $\Omega_a$ and the surrounding regions as $\Omega_b$. The Li concentration in $\Omega_a$ (which is denoted as $x^a$) increases faster than $x^b$ (the Li concentration in $\Omega_b$) and enters the unstable spinodal range before its surroundings. Subsequently, $\Omega_a$ experiences a concentration surge, and $x^a$ rapidly traverses from the lower spinodal to the upper spinodal point. This process can be illustrated by the magenta arrow in Fig. 4A, wherein the chemical potential function is non-monotonic because of the two-phase nature of LFP. Thereafter, when $x^b$ enters the spinodal composition range (following the cyan arrow in Fig. 4B), $x^b$ decreases (following the magenta arrow in Fig. 4B) because of the driving force toward the equilibration of the chemical potentials of the two regions. The value of $x^a$ can drop to the upper spinodal point (as indicated by the black arrow in Fig. 4B), followed by a rise back to the lithiated state. In this case, the degree of concentration reversal is small and limited to the upper spinodal point when the chemical potential function is assumed to be the same for all regions in the particle. However, the experiment presented above showed a much larger concentration reversal in some regions, such as the local domain A in Fig. 3I, wherein the highly lithiated region (with concentration of ~0.6) experienced an abrupt decrease to the Li-poor state (with concentration of ~0.1).

To explain such a large concentration drop, we propose a modification to the chemical potential function of $\Omega_a$ by making it higher than that of $\Omega_b$ near the upper spinodal point. The red ($\mu^0$) and blue ($\mu^a$) curves in Fig. 4 (C and D) represent the chemical potential functions.
for $\Omega_a$  and $\Omega_b$, respectively. In this scenario, $x^a$ is able to traverse back to the delithiated state (following the magenta arrow in Fig. 4D) as $x^b$ crosses the spinodal range (following the cyan arrow in Fig. 4D), after the fast lithiation of $\Omega_a$, seen in Fig. 4C. This large concentration drop is indicated by the black arrow in Fig. 4D. Such a large concentration drop during lithiation of $\Omega_a$ seen in Fig. 4C. This large concentration drop is indicated by the black arrow in Fig. 4D. Such a large concentration drop during lithiation of the particle, spanning over the entire spinodal range as observed in the experiment, is only possible when the chemical potential functions near the upper spinodal point are different.

To verify the proposed mechanism for the large concentration reversal due to the variation in local chemical potential functions, we performed a set of 3D phase-field modeling (43) to simulate the process of intercalation. The main results are provided in Fig. 5. In this model, the evolution of the system is described by a governing equation based on the transport resulting from the chemical potential gradient. The computational domain represents a portion of a particle that contains two distinct regions, $\Omega_a$ and $\Omega_b$, which are assumed to be static and have different free energy functions and thus different chemical potential functions (the red and blue curves in Fig. 5A). These functions are selected such that the simulated Li concentration evolution resembles the experimental observation. The function of $\mu^a$ deviates from $\mu^b$ in a degree larger than in Fig. 4 (C and D). This assumption is not unreasonable because the Li free energy functions are influenced by impurities and defects, which may cluster on the nanoscale regions. Thus, the free energy function could be affected over the entire Li concentration range, not just near the upper spinodal point. Note S1 provides information and discussion about the presence of clustering of anti-site defects, supported by multimodal characterizations (figs. S11 and S12). Anti-site defects can form early due to high mobility of Fe ions in FP (44). However, when the particle is fully lithiated, the migration barrier of the Fe ion in LFP is so high (1.2 eV) that the Fe ion becomes essentially immobile (44). Because we have no information on Fe mobility at the intermediate states, we take the simplifying assumption of static domains in light of the fact that little information is available on the dynamics of defect formation and clustering.

In a simplified configuration, several rectangular cuboids (representing $\Omega_a$) were encompassed by $\Omega_b$ (Fig. 5B). In the early stage, the equilibrium of Li chemical potentials (as indicated by the black dashed line in Fig. 5A) will drive Li concentration in $\Omega_a$ (denoted as $x^a_0$) to be higher than that in $\Omega_b$ (denoted as $x^b_0$) (see Fig. 5, A and C). Once Li concentration in $\Omega_b$ exceeds the lower spinodal ($x^b_1$), $\mu^b$ decreases (following the cyan arrow in Fig. 5A) because of the nonmonotonic form of the chemical potential function. Driven by the difference in chemical potentials, $x^a_0$ decreases to $x^a_2$.

Fig. 5. Simulation of the localized concentration reversal within a single-crystalline particle using a phase-field model. (A) Chemical potential functions $\mu^a$ and $\mu^b$ versus normalized Li concentration ($x$) for the fast-lithiating regions $\Omega_a$ and surrounding regions $\Omega_b$, respectively. (B to E) Snapshots of projected Li concentration along the [010] direction (left column) and the corresponding 3D view of the simulated concentration distribution (right column) at different stages of lithiation. The color scale represents Li concentration. Several cuboids marked by white boxes in (B) are assumed to be $\Omega_a$ with the modified chemical potential function, $\mu^a$. The normalized Li concentrations of the $\Omega_a$ and $\Omega_b$ in (A) are also labeled in (C) to (E). (F) Evolution of averaged Li concentration over different sampling sizes as labeled with domains 1 and 2 in (B), which was extracted from movies S2 and S3. Domain 1 is selected to be inside $\Omega_a$, whereas domain 2 consists of $\Omega_b$ and a part of surrounding $\Omega_a$. The averaged concentration of domain 1 is plotted as the magenta curve that exhibits similar behavior as the experimentally examined FP nanoparticle during lithiation (Fig. 3J).
(the magenta arrow in Fig. 5A), corresponding to Fig. 5 (D and E, respectively). Consequently, \( x^0 \) undergoes a nonmonotonic evolution during the lithiation of the nanoparticle, as shown by the magenta curve in Fig. 5F. This concentration reversal is in agreement with that observed experimentally in Fig. 3, and thus, the simulation demonstrates that the redistribution of local Li concentration within the nanoparticles can be driven by the difference of chemical potentials between regions having different free energy functions.

The dependence of the reversal on the size of data sampling area (as illustrated in Fig. 3) can also be explained through the phase-field simulations. With an increased size of sampling volume (for example, domain 2), the lithiation of \( \Omega_N \) offsets the concentration reversal in domain 1, resulting in a nearly monotonic overall increase in concentration (as shown by the cyan curve in Fig. 5F), which supports the experimental observation depicted in Fig. 3).

The observation of concentration reversal in the present study serves as a critical indication of the intrinsic tendency of the FP-LFP two-phase transformation even in the absence of the distinctive phase boundaries. The nonmonotonic chemical potential function leads to the decrease of the Li chemical potential in \( \Omega_N \) as \( x^0 \) increases within the spinodal range, thus inducing \( \Omega_N \) to delithiate even though overall the particle is lithiating. Intrinsic solid-solution materials, with monotonic chemical potential functions, lack the necessary driving force to reduce Li concentration of lithiated regions. Hence, the experimental observations of concentration reversal confirm that LFP nanoparticles lithiate through a metastable, nonequilibrium solid-solution pathway.

Strain energy, present due to the inhomogeneous Li distribution, may be one of the factors that would affect the amplitude of reversal. The strain energy density estimated using Li concentration distribution shown in Fig. 5D and the calculated elastic moduli and lattice parameters of FP and LFP (45) are mostly well below 5 meV per Li site, although the maximum value can approach 9 meV per Li site in a small region (fig. S13). The strain energy density overall is smaller than the calculated energy barrier for the solid solution between FP and LFP of \( \approx 15 \) to 20 meV (20). As a result, the observed reversal phenomenon will likely remain qualitatively unchanged by strain energy. Furthermore, kinetically, it is possible that strain energy can change the migration barrier of Li (46). However, local modifications of the mobility due to strain would not induce the concentration reversal in the absence of the thermodynamic driving force. Overall, we believe that strain effect is unlikely to be the sole origin of concentration reversal.

The complex, dynamic intercalation processes observed in this study can occur in other intercalation electrode materials containing regions with different free energy functions. Although the variation in the free energy functions may appear to originate from anti-site defect clusters in LFP, similar phenomena might be observed when dopants (8), impurities, or other types of defects (47) form clusters and alter the local Li chemical potentials in other intercalation-type electrodes. However, such a phenomenon is expected to be observable only at an extremely small scale (10 nm or less), because it will be smoothed out after averaging on a larger scale. Therefore, the experimental confirmation will require extremely high-resolution techniques such as the in situ imaging coupled with GPA analysis. Additional details such as the dynamic formation of defect clusters can have an impact on the exact behavior of the concentration reversal, which may depend on the lithiation rate. To evaluate such effects quantitatively, further in situ observations of the evolution of defects within a single nanoparticle at different rates are required. However, achieving the required resolution is extremely challenging and it will be a subject of future study.

**CONCLUSION**

We investigated the intercalation dynamics in individual FP nanoparticles through real-time tracking of lithiation-driven structural evolution at unprecedented resolution. The local Li intercalation via kinetically favorable solid-solution pathway was unveiled at scales varying from single nanometer to tens of nanometers, and up to the entire FP nanoparticles. Despite many studies of nonequilibrium intercalation and phase transformations in nanoparticulate Li₄FePO₄ (11, 19–21, 23, 24, 36, 48), only through this work was inhomogeneous intercalation within a single nanoparticle identified. In contrast to the traditional assumption of monotonic Li incorporation within a single nanoparticle, this study revealed an unexpected reversal of the local Li concentration in nanosized domains within a particle. The discovery of inhomogeneous intercalation and localized concentration reversal of Li during intercalation into a single nanoparticle adds new insights into the existing knowledge of nonequilibrium electrochemical reactions in intercalation-type electrodes (11, 20, 23, 24).

On the basis of an assumption that different regions have different local free energy, a theory was proposed to explain the thermodynamic origin of the observed reversal phenomenon. With the thermodynamic driving force toward equilibration of the different Li chemical potentials, the local Li concentration in some regions rises by absorbing Li from its surroundings and subsequently drops when the surroundings reach spinodal composition and experience a large driving force toward lithiation. The findings from this study provide new perspective on the local dynamics of electrochemically driven phase transformations in intercalation-type battery electrodes.

**MATERIALS AND METHODS**

**Materials synthesis and electrochemical measurements**

LFP nanoparticles were synthesized using the solvothermal method (35). LiOH aqueous solution (450 ml of 1 M) was mixed with H₃PO₄ (150 ml of 1 M) and polyethylene glycol (600 ml) to form a milk-white suspension. Then, FeSO₄ solution (300 ml of 0.5 M) was added into the white suspension while stirring. The mixture was transferred into an autoclave, which was then held at 180°C for 9 hours. After cooling to room temperature, the product was collected and washed with pure water three times. The final product was dried under vacuum at 80°C for 12 hours. FP was prepared by chemical delithiation of LFP with nitric acid (47).

**Structure characterization**

The LFP and FP nanoparticles were characterized by x-ray using beamline X14A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The TEM and annular dark-field (ADF) images were recorded in a JEOL 2100F microscope at 200 kV with a 0.23-nm point-to-point spatial resolution. The HRTEM and high-angle ADF (HAADF) images, in situ ED patterns, and EELS spectra were
recorded from the lithiated samples using a JEOL ARM 200F microscope equipped with two spherical aberration correctors, a cold field emission electron source, and a high-resolution dual-EELS spectrometer. The simulated HAADF image was calculated on the basis of the multislice method with frozen phonon approximation. During in situ ED measurements, two diffraction patterns were recorded per second, which is the same as the frequency in time-resolved XRD measurement (49). Alignment was performed in selected nanoparticles that were basically projected parallel or perpendicular to the [010] direction. The electron beam damage was minimized by spreading the electron beam to the largest beam diameter to ensure that the in situ ED measurement revealed the state of phase transformation without artifacts.

**In situ HRTEM experiments**

For the in situ HRTEM experiments, we used a similar design of the in situ cell as described by Wang et al. (17). The FP nanoparticles were loaded onto 10-nm-thick amorphous carbon films in the TEM half-grids. The carbon film has a similar role as the carbon black used in typical FP-C electrodes, acting as the media for transporting electrons and ions. A tungsten tip was used to scratch fresh Li metal from a cut Li metal surface in an argon glove box and attached to a piezo-driven biasing probe built into the TEM–scanning tunneling microscopy sample stage (Nanofactory Instruments AB). All the components were sealed in an argon glove box and transferred into the TEM column using an Ar-filled bag. As shown in Fig. 1B, the biasing probe touched the carbon, and a negative bias versus TEM half-grid (above 3 V) was applied to initiate the reaction. No reaction or current flow occurred before applying the bias, or with a lower biasing potential. The battery consisted of a typical FP-C electrodes, acting as the media for transporting electrons and ions. A tungsten tip was used to scratch fresh Li metal from a cut Li metal surface in an argon glove box and attached to a piezo-driven biasing probe built into the TEM–scanning tunneling microscopy sample stage (Nanofactory Instruments AB). All the components were sealed in an argon glove box and transferred into the TEM column using an Ar-filled bag. As shown in Fig. 1B, the biasing probe touched the carbon, and a negative bias versus TEM half-grid (above 3 V) was applied to initiate the reaction. No reaction or current flow occurred before applying the bias, or with a lower biasing potential. The battery consisted of a TEM grid (current collector), FP-C (cathode), and Li metal (anode). A thin passivation layer of LiNxOy on the surface of the Li metal acted as the solid electrolyte (17).

**Geometric phase analysis**

GPA is a robust image-processing technique based on HRTEM images (50–52). Here, we used it to map the change in lattice spacing during phase transformation. The optical distortions caused by the projector lenses of the microscope (33) were corrected for all the GPA maps.

By applying a small mask (with the shape of one Brillouin zone) around a local Fourier component of the lattice fringes, \( \mathbf{g} \), in the Fourier transform of a HRTEM image, we obtained the inverse Fourier transform \( H_g(\mathbf{r}) \) as

\[
H_g(\mathbf{r}) = A_g(\mathbf{r}) \exp \{ ip_g(\mathbf{r}) \}
\]

where \( A_g(\mathbf{r}) \) and \( p_g(\mathbf{r}) \) are the amplitude and phase, respectively, and \( \mathbf{r} \) is the position of the lattice fringes in the real space. \( P_g(\mathbf{r}) \) was used to determine the positions of the lattice fringes in real space. \( H_g(\mathbf{r}) \) can be related to the usual procedure to produce a Bragg filtered image, \( B_g(\mathbf{r}) \), which is to place a mask around the spots \( \pm \mathbf{g} \) in the Fourier transform of the image and then to take its inverse Fourier transform

\[
B_g(\mathbf{r}) = H_g(\mathbf{r}) \exp \{ 2\pi i \mathbf{g} \cdot \mathbf{r} \} + H_g(\mathbf{r}) \exp \{ -2\pi i \mathbf{g} \cdot \mathbf{r} \}
\]

Because the HRTEM image intensity \( I(\mathbf{r}) \) is a real function, \( H_g(\mathbf{r}) = H_g^*(\mathbf{r}) \), Eq. 3 becomes

\[
B_g(\mathbf{r}) = 2Re [H_g(\mathbf{r}) \exp \{ 2\pi i \mathbf{g} \cdot \mathbf{r} \}] = 2A_g(\mathbf{r}) \cos \{ 2\pi \mathbf{g} \cdot \mathbf{r} + P_g(\mathbf{r}) \}
\]

For an image with perfectly regular set of fringes

\[
B_g(\mathbf{r}) = 2A_g(\mathbf{r}) \cos \{ 2\pi \mathbf{g} \cdot \mathbf{r} + C_g \}
\]

where \( C_g \) is a constant. For an image with varying fringe spacing, the equation is

\[
B_g(\mathbf{r}) = 2A_g(\mathbf{r}) \cos \{ 2\pi \mathbf{g} \cdot \mathbf{r} + 2\pi \Delta \mathbf{g} \cdot \mathbf{r} \}
\]

where \( \Delta \mathbf{g} \) is the local departure from the ideal reciprocal lattice vector, \( \mathbf{g} \). Comparing this equation with Eq. 4, we find that

\[
P_g(\mathbf{r}) = 2\pi \Delta \mathbf{g} \cdot \mathbf{r}
\]

By taking the gradient of Eq. 7, we obtain

\[
\Delta \mathbf{g} = \nabla P_g(\mathbf{r})/2\pi
\]

If we use FP as the reference lattice with lattice parameter \( a_{\text{ref}} \) along the \( a \) direction, whereas the local lattice spacing in the image is \( a(\mathbf{r}) \), by choosing \( g = 100 \) in Fig. 3A, we obtain

\[
\Delta g = \frac{1}{a(\mathbf{r})} - \frac{1}{a_{\text{ref}}} = - \frac{a(\mathbf{r}) - a_{\text{ref}}}{a(\mathbf{r}) a_{\text{ref}}} = - \frac{\Delta a}{a(\mathbf{r}) a_{\text{ref}}}
\]

Combining Eqs. 8 and 9, the change in the lattice spacing \( a(\mathbf{r}) \) as a function of the position and time can be expressed as

\[
\Delta a(\mathbf{r}, t) = - \frac{a(\mathbf{r}) a_{\text{ref}}}{2\pi} \nabla P_g(\mathbf{r}, t)
\]

Using Vegard’s law, the Li concentration shown in Fig. 3 (B to I) can be calculated to equal

\[
\frac{\Delta a}{a_{\text{LFP}} - a_{\text{ref}}} = - \frac{a a_{\text{ref}}}{2\pi (a_{\text{LFP}} - a_{\text{ref}})} \nabla P_g(\mathbf{r}, t)
\]
Phase-field simulations
A phase-field method was used to simulate the Li concentration evolution during lithiation. The concentration evolution is assumed to be governed by the Cahn-Hilliard equation (43)

\[
\frac{\partial \chi}{\partial t} = \nabla \cdot M \nabla \mu = \nabla \cdot M \nabla (\mu - \nabla \cdot x \nabla x) \tag{12}
\]

where \(x\) is the normalized Li concentration, \(t\) is the time, \(M\) is the transport mobility, \(\mu\) is the total Li chemical potential including the gradient energy penalty, \(\mu\) is the chemical potential defined as the derivative of the bulk free energy with respect to concentration, and \(\kappa\) is the gradient energy coefficient. Equation 12 was nondimensionalized for the simulations, with a length unit \(l = 1\) nm and a mobility unit \(M = 5.32 \times 10^{-15}\) cm\(^2\)/s (evaluated according to the diffusivity of Li of \(3.2 \times 10^{-11}\) cm\(^2\)/s). Thus, the time unit is \(1.875 \times 10^{-3}\) s (\(t = \frac{t}{M}\)). In this model, we used two anisotropic (dimensionless) transport parameters for \(\Omega_\omega\) and \(\Omega_\beta\):

\[
\mu^\omega = 2.2(1 - 2x) + \ln(x/(1 - x)) + 0.35 \in \Omega_\omega, \tag{13a}
\]

\[
\mu^\beta = 3.3(1 - 2x) + \ln(x/(1 - x)) \in \Omega_\beta. \tag{13b}
\]

These two functions have the same form as those based on the regular solution model and are shown as the red and blue curves in Fig. 5A. Note that the regular solution chemical potential function is normalized such that the entropy term has a coefficient of unity. We assumed that the interface energy in the particle was isotropic and set \(\kappa_b\) and \(\kappa_a\) equal to 200 and 2, respectively, to generate comparable interfacial energy in the particle. The dimensionless grid spacing was set to be one. The Li concentration in the particle was initially uniform at 0.04 for the ease of numerical simulations. Because we only focused on the evolution of Li concentration inside the particle, instead of the voltage response during an electrochemical reaction, we did not use the Butler-Volmer equation for the insertion flux. Instead, the Li insertion rate was assumed to be proportional to the Li chemical potential difference across the particle surface. Thus, the flux boundary conditions for Li insertion were set as \(J^b_s = -K(\mu - \mu^0)\) on the two computational domain boundaries that are perpendicular to the \(b\) axis, where \(K\) is the surface reaction rate constant and \(\mu^0\) represents the Li chemical potential outside the computational domain. The value of \(\mu^0\) was kept constant, similar to a simplified constant voltage loading condition (53). The dimensionless value of \(K\) was set to be \(3.125 \times 10^{-3}\) to ensure near-equilibrium insertion dynamics in which the Li concentration evolution in the particle is governed by thermodynamics and diffusion kinetics. The remaining four boundaries were assumed to be within the LFP particle. Thus, no flux boundary conditions were imposed at these boundaries. Therefore, our phase-field model considered both thermodynamic driving force as well as kinetics simultaneously and consistently.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/1/eaao2608/DC1

movie S1. An in situ TEM movie showing the evolution of the ED patterns projected along the [010] direction.

movie S2. A simulation movie showing the evolution of projected Li concentration along the [010] direction.

movie S3. A 3D view movie showing the evolution of simulated Li concentration distribution in different local regions.

fig. S1. Morphology and structure of FP and LFP nanoparticles.

fig. S2. Electrochemical performance of FP nanoparticles tested in regular coin cells.

fig. S3. A bright-field TEM image showing a single-crystalline FP nanoparticle (in the central region), being tilted to [010] direction for in situ ED measurements (Fig. 2).

fig. S4. The evolution of ED intensity profiles of diffraction spot (001) versus distance from the central spot (000), shown with original data (dots), and fitted ones (solid lines) by weighted Gaussian and Lorentzian functions.

fig. S5. Electron energy-loss spectra of Fe-L\(_2,3\) and O-K edges from the FP nanoparticle (shown in Fig. S1), with original data (dots), and fitted ones (solid lines) by weighted Gaussian and Lorentzian functions.

fig. S6. HRTEM images from a single particle (oriented along [010]) during lithiation (as in Fig. 3) before and after lithiation during in situ ED measurements.

fig. S7. Evolution of ED intensity profiles of (100) and (001) diffraction spots in the FFT patterns obtained from the HRTEM images in Fig. S6, in comparison to that obtained from in situ ED measurements.

fig. S8. Local lattice displacement in FP due to lithiation.

fig. S9. Intensity profiles of the Li concentration distribution showing continuous variation of the Li concentration between the neighboring Li-rich and Li-poor regions.

fig. S10. Evolution of Li concentration averaged at the lower left and upper left corners of region B in Fig. 3 (B to I).

fig. S11. Synchrontron XRD patterns in comparison to that obtained by Retveld refinements, from pristine LFP, chemically delithiated FP, and electrochemically lithiated LFP.

fig. S12. Inhomogeneity of anti-site defects within the electrochemically lithiated nanoparticles (LFP).

fig. S13. Calculated strain energy density on the surface of the nanoparticle (shown in Fig. 3) before and after lithiation during in situ ED measurements.

fig. S14. Evolution of Li concentration averaged over different sampling sizes (as labeled with domains 1 and 2 in Fig. S8), with low and high anisotropic ratios of Li mobility along the three crystalline directions.

Note that the Li diffusivity along the \(b\) axis in the \(\Omega_\beta\) region is approximately 100 times that in \(\Omega_\omega\), because diffusivity is related to transport mobility by \(D = M \partial \mu/\partial x\), where \(x\) is the Li fraction, and \(\partial \mu/\partial x\) values are different in the two regions. In addition, because of the presence of high density of defects, it is possible that the Li mobility along \(a\) and \(c\) directions is larger than that along the \(b\) direction. In such cases, the amplitude of concentration reversal will be increased because of enhanced cross-channel Li transport. This effect was observed in the parametric study, as shown in fig. S14 and note S2.

A standard finite difference scheme was used for spatial discretization, and the forward Euler explicit time-stepping scheme was used for temporal evolution. A rectangular computational domain with dimensions of \(60 \times 60 \times 30\) grid points along the \(a\), \(b\), and \(c\) crystalline orientations, respectively, was used in the simulations. The dimensionless grid spacing was set to be one. The Li concentration in the particle was initially uniform at 0.04 for the ease of numerical simulations.

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