Visualizing non-equilibrium lithiation of spinel oxide via *in situ* transmission electron microscopy

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Spinel transition metal oxides are important electrode materials for lithium-ion batteries, whose lithiation undergoes a two-step reaction, whereby intercalation and conversion occur in a sequential manner. These two reactions are known to have distinct reaction dynamics, but it is unclear how their kinetics affects the overall electrochemical response. Here we explore the lithiation of nanosized magnetite by employing a strain-sensitive, bright-field scanning transmission electron microscopy approach. This method allows direct, real-time, high-resolution visualization of how lithiation proceeds along specific reaction pathways. We find that the initial intercalation process follows a two-phase reaction sequence, whereas further lithiation leads to the coexistence of three distinct phases within single nanoparticles, which has not been previously reported to the best of our knowledge. We use phase-field theory to model and describe these non-equilibrium reaction pathways, and to directly correlate the observed phase evolution with the battery’s discharge performance.
In this work, we investigate how non-equilibrium intercalation and conversion reactions proceed by studying the lithiation process in real time. X-ray scattering or Mössbauer spectroscopy is most often used to identify the phase transformations that occur in nanosized electrode materials\cite{16,19}, but these techniques have the disadvantage of providing only average information, and generally they lack the ability to probe reaction kinetics in real time. Critically, it is important to undertake lithiation studies in situ, as ex situ studies may provide inaccurate information due to changes that may occur during removal of the electrode materials from an actively lithiated condition\cite{22,27}. In contrast, transmission electron microscopy (TEM) allows direct, real-time information to be obtained from structures at the atomic scale.

The need for in situ observations of this type has been increasingly recognized, and thus there have been many recent reports of the use of in situ TEM techniques to study alloying and conversion reactions\cite{28-38}. However, directly visualizing phase transitions that occur during intercalation reactions is challenging because the volume change that occurs during this type of reaction is negligible\cite{39-42}. This prevents the use of standard diffraction contrast imaging techniques. In this work, we utilize a strain-sensitive, bright-field scanning TEM (BF-STEM) imaging technique to overcome this challenge. This approach allows us to observe the phase changes that occur in monodisperse Fe$_3$O$_4$ nanoparticles in situ during the intercalation reaction, and follow the subsequent conversion reaction directly. By integrating ex situ synchrotron X-ray and in situ TEM approaches, we capture in detail the mechanisms by which lithiation occurs and relate this directly to the reaction kinetics. Furthermore, we support these observations with both density functional theory (DFT) calculations and non-equilibrium phase-field theory to describe the atomistic processes from first principles and phenomenological perspective, respectively. This work highlights the importance of exploiting advanced TEM techniques to reveal reaction inhomogeneities at the nanoscale.

### Results

#### Material structures and electrochemical properties.

The as-synthesized Fe$_3$O$_4$ nanoparticles are ca. 80 nm truncated octahedrons, as shown in Fig. 1a and Supplementary Fig. 1. Atomic-resolution high-angle annular dark-field (HAADF) STEM images (as in Fig. 1b) indicate that the pristine Fe$_3$O$_4$ nanoparticles are single-crystalline with the inverse spinel structure (Fd$ar{3}$m space group) and terminated with {111} crystal planes. To characterize the electrochemical performance, voltage profiles at different C-rates (1C, C/10 and C/200, or 926 mA g$^{-1}$, 92.6 mA g$^{-1}$ and 4.63 mA g$^{-1}$, respectively) are shown in Fig. 1e. The first discharge capacity is 1.080 mA h g$^{-1}$ at C/200, and it decreases to 0.916 mA h g$^{-1}$ and 0.914 mA h g$^{-1}$ for C/200 and C/10, respectively, close to the theoretical capacity of 0.926 mA h g$^{-1}$. The capacity excess in the initial discharge is generally believed due to side reactions involving electrolyte decomposition and formation of solid electrolyte interphases\cite{43-45}, while the following cyclic tests show a rate performance (Supplementary Fig. 2) that is comparable to previous reports\cite{10-12}. After full discharge (lithiation), the electrode materials have changed their structure and morphology dramatically to form a nanocomposite consisting of ultrathin (<5 nm) Fe nanoparticles and an amorphous Li$_2$O matrix phase (Fig. 1c), as confirmed by electron diffraction (Fig. 1d). It is noted that two distinct plateaus appear in the C/200 discharge curve, corresponding to the intercalation reaction and conversion reaction, respectively\cite{13-15,17}, whereas the intercalation plateau is absent from the relatively faster discharge curves at rates of 1C and C/10. This can be due to enhancements in the reaction
kinetics that can occur at high discharge current densities (such as voltage polarization). To justify this hypothesis, we employed the galvanostatic intermittent titration technique (GITT)\(^{46}\) for a discharge cycle at C/10 to measure the OCV profile: this reflects the equilibrium redox potentials at different states of charge (SOCs). Figure 1f clearly indicates the voltage polarization between the OCV and regular discharge profile, and confirms the existence of an intercalation plateau which is related to the charge rate. The intercalation process can generally be expressed as equation (2):

\[
xLi + Fe_3O_4(\text{spinel}) \rightarrow Li_xFe_3O_4(\text{rocksalt})
\]

where \(x\) is the lithium content per formula. For an intercalation reaction, \(x\) is supposedly between 0 and 2 (refs 16–18), and its upper limit depends on the total amount of lithium ions accommodated at the tetragonal 8a sites\(^{16,17}\). Further lithiation would trigger the conversion reaction. This is also confirmed by high-resolution TEM (HRTEM) imaging of \textit{ex situ} lithiated...
Li$_2$Fe$_3$O$_4$ with Li content $x = 2, 3, 4, 5, 6, 7, 8$ (Supplementary Fig. 3). These HRTEM images and selected area electron diffraction (SAED) patterns show the transition from rocksalt Li$_x$Fe$_3$O$_4$ to Fe + Li$_2$O composite in a gradually proceeding manner. Since the intercalation reaction only involves Li content $x < 2$, it is crucial to focus our study on the first half of the lithiation. To study the intercalation process further, we utilized synchrotron X-ray diffraction (SXRD) to identify the phase changes at various SOCs of $x = 0, 0.5, 1, 1.5, 2, 3$ and $4$, as shown in Fig. 1g,h. The series of SXRD patterns show that the electrode materials transfer from spinel structure to rocksalt structure with increasing Li composition (detailed indexing is presented in Supplementary Fig. 4). From the enlarged patterns in Fig. 1h, we indeed identified the two stable Fe$_3$O$_4$ and LiFe$_3$O$_4$ phases. The nanosized Fe phase that resulted from the conversion reaction cannot be captured by SXRD even up to $x = 4$; however, its presence was confirmed using TEM (Supplementary Fig. 5). These observations clearly indicate that SXRD—due to its lack of sensitivity in detecting nanoscale particles, and its averaging characteristics—is not able to precisely track the phase evolution at very high spatial resolution. In addition, the absence of an intercalation plateau in the cycling profiles of 1C and C/10 implies that the intercalation process is by-passed at high rates. Although the SXRD results clearly show the existence of a rocksalt intermediate phase, which arises from the intercalation reaction, the presence of this phase might also be due to a possible structure relaxation and phase separation that occurs post-mortem. Effects of this type have been reported in LFP system, where ex situ characterization is shown to inaccurately describe the reaction processes that are occurring$^{21}$. In addition, the intercalation phase transition can either follow a two-phase model or solid-solution process depending on the details of the reaction kinetics, a process which cannot be resolved from the ex situ study. To solve these issues, we have utilized in situ electron microscopy approaches to determine which reaction pathways occur in spinel oxide.

**Phase evolution by in situ electron diffraction.** We utilized a dry cell set-up for our in situ TEM investigation$^{36-38}$. This approach can precisely track the phase evolution at very high spatial resolution. Since there are no liquid organic electrolyte involved in the reactions, to verify the consistency in the phase transitions between the ex situ and in situ experiments, we tracked the dynamical phase evolution using in situ electron diffraction throughout the entire lithiation process, as shown in Fig. 2a and Supplementary Movie 1. The radially integrated intensity profiles from a series of time-sequenced SAED patterns are plotted as a function of lithiation time, with the intensity represented by false colours (Fig. 2a). It is obvious that both the position and intensity of the Bragg reflections change as the lithiation proceeds, verifying the overall phase transformation from pristine Fe$_3$O$_4$ to the eventual Fe and Li$_2$O composite (and in the same manner as the ex situ results). Using the intensity profiles of Fe$_3$O$_4$ (311) and Fe (110) SAED peaks as a measure, the gradual evolution of the phase transformation becomes clear, as depicted in Fig. 2b. It is also worth noting that the Bragg peaks of the Fe$_3$O$_4$ phase display a negative shift in reciprocal space (as indicated by arrows in Fig. 2a) during the initial stage of lithiation (up to $\sim 1,000$ s), which corresponds to an increase in the lattice parameter as Li$^{2+}$ ions are inserted into the Fe$_3$O$_4$ lattice (Fig. 2c). This lattice parameter increase is quantitatively consistent with the phase transition from Fe$_3$O$_4$ to LiFe$_3$O$_4$, as extracted from our SXRD measurements. After $\sim 1,000$ s, the lattice expansion...
becomes more severe, indicating that the subsequent lithiation was dominated by the conversion reaction, as per equation (3).

\[(8 - x)\text{Li} + \text{Li}_x\text{Fe}_3\text{O}_4 \rightarrow 4\text{Li}_2\text{O} + 3\text{Fe} \quad (3)\]

**Visualization of two-step lithiation by in situ BF-STEM.** After verifying that the phase transformation occurs using *in situ* SAED, we performed an *in situ* BF-STEM observation to follow how the structure evolves during the entire lithiation process in real space, as shown in Fig. 3a and Supplementary Movie 2. The time-sequenced BF-STEM images record the intensity of the transmitted electrons scattered to lower angles, as well as the direct beam (involving the most coherent electron scattering). This signal is strain sensitive and thus enables direct visualization of the small lattice changes that occur during the intercalation process (Supplementary Fig. 6). We show that this is essential observing intercalation reactions in real time. This is in contrast to other, more conventional imaging techniques (such as HAADF-STEM or BF/DF TEM) which do not have the requisite image sensitivity to directly observe this process (sensitivity to strain is not satisfied due to incoherent contrast or bending contour). The first intercalation step follows the reaction described in equation (2) to generate the lithium-inserted Li$_x$Fe$_3$O$_4$ phase (shown with a lighter contrast). These regions will be further lithiated in the subsequent conversion reaction, which is also accompanied by the extrusion of ultrafine metallic Fe nanoparticles to form a composite with the amorphous Li$_2$O. For better visualization, we use false colours to distinguish the pristine Fe$_3$O$_4$ (red), Li-inserted Fe$_3$O$_4$ (blue) and completely conversion composite (green) phases and their evolution as a function of time. This was also verified using electron energy-loss spectroscopy (EELS) in STEM (Supplementary Fig. 7). We note that, under realistic electrochemical environment, the lithiation process shows a non-equilibrium reaction pathway, that is, the conversion reaction starts to take place before the intercalation completely finishes. This may be likely due to the fact that the diffusion of lithium on the Fe$_3$O$_4$ particle surface is faster than that through the lithiated Li$_x$Fe$_3$O$_4$ phase, which can cause a sufficiently large lithium concentration at the particle surface and thereby trigger the conversion reaction to happen at an early stage (but still after the intercalation reaction). It is obvious that both intercalation and conversion reactions follow a ‘shrinking-core’ mode, proceeding from the outer surface to the inner region. Specifically, the initial intercalation trajectory does not exhibit any preferential directions, in accord with the zigzag Li$^+$ diffusion paths in three-dimensional (3D) tunnels, whereas the subsequent conversion tends to propagate through the outer facets, that is, {111} planes. As an approximate measure of reaction kinetics, we quantified the projected areas of the three phases versus the lithiation time, displayed in Fig. 3b. This figure shows that the propagation speed of the intercalation process is about 1 order of magnitude faster than the following conversion reaction (Fig. 3c). We note that these measurements are from one single particle, where the electrochemical conditions are supposed to be identical. This is consistent with the fact that full conversion needs multiple Li-ion transfers, when compared with the intercalation process. We do not believe this to be an effect resulting from local electrochemical inhomogeneity.

**HRTEM characterization.** For a fundamental understanding of the intercalated phase, we conducted HRTEM imaging to track the atomic structure changes for both *in situ* and *ex situ* scenarios, as shown in Fig. 4. A new phase with the rocksalt structure was observed *in situ* as Li$^+$ ions were inserted into the spinel Fe$_3$O$_4$ phase (Fig. 4a,b). Using two sets of diffraction spots from the fast Fourier transform (FFT, Fig. 4a insets), we can separately map the distribution of the spinel (red) and rocksalt (green) phases and thus visualize the propagation of the intercalation front in the

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**Figure 3 | In situ observation of two-step phase transformation during lithiation.** (a) BF-STEM image series showing phase evolution during lithiation. The overlaid false colours indicate different phases: pristine Fe$_3$O$_4$ (red), Li-inserted Li$_x$Fe$_3$O$_4$ (blue) and Fe + Li$_2$O composite after conversion (green). Scale bar, 20 nm. The sample was lithiated at a rate of ~2,700 mA g$^{-1}$. (b) Projected areas of the three phases as a function of time. (c) Propagation speed of intercalation and conversion as a function of time.
Rocksalt bars: (8b and 48f sites to form Li$_2$Fe$_3$O$_4$ phase without Fe extrusion$^{16,17}$. That the excess Li ions (up to $x = 1$) during lithiation, and also repel the adjacent Fe cations from the 8a to the 16c sites to form Li$_x$Fe$_3$O$_4$ crystals with the rocksalt structure, with lithium composition up to $x = 1$. It is also noted from previous reports that the excess Li ions (up to $x = 2$) could possibly insert into the 8b and 48f sites to form Li$_x$Fe$_3$O$_4$ phase without Fe extrusion$^{16,17}$. However, this particular phase was not experimentally identified from TEM observations. Nevertheless, the intercalation process goes through a two-phase mode and forms an intermediate phase of Li$_x$Fe$_3$O$_4$ (refs 16–18). Thereafter, the conversion reaction occurs and the Li$_x$Fe$_3$O$_4$ phase is decomposed into Li$_2$O and metallic Fe nanocrystals, which can be observed as the speckles in Fig. 4b,d. Combining both in situ TEM imaging and ex situ SXRD results, we now can conclude that the intercalation proceeds in a two-phase ‘nucleation and growth’ manner, resulting in sharp interfacial boundaries between the spinel and rocksalt phases, as expressed in equation (2).

**First principles calculations and phase-field modelling.** DFT computation has been performed to calculate the voltage profile of the lithiation process under the thermodynamic equilibrium condition$^{48–52}$. The calculated reaction pathway has multiple voltage plateaus (green dashed curve in Fig. 5a) with intermediate phases, such as LiFeO$_2$, Li$_2$FeO$_2$ and Li$_2$FeO$_4$ (Fig. 5b). Given that the LiFeO$_4$ is an intermediate phase experimentally observed from SXRD, our DFT calculations also considered a two-step reaction route (red curve in Fig. 5a), including the intercalation plateau ($\text{Li} + \text{Fe}_3\text{O}_4 \rightarrow \text{LiFe}_3\text{O}_4$) and the conversion plateau ($\text{LiFe}_3\text{O}_4 \rightarrow \text{Li}_2\text{O} + \text{Fe}$). The ground-state LiFe$_3$O$_4$ structure as illustrated in the inset crystal models of Fig. 5a possesses a similar structural framework (that is, $[\text{Fe}]_{16d}\text{O}_2$ octahedron) that was inherited from the spinel Fe$_3$O$_4$ structure. Consistent with the ground-state LiFe$_3$O$_4$ structure calculated in the DFT computation, Li ions insert into the octahedral 16c openings, and repel the nearby 8a Fe ions to the other surface-sharing 16c site, which forms the structure identical to that observed in the HRTEM images in Fig. 4. In addition, since the octahedral 16c sites are interconnected as a 3D channel, the initial intercalation would proceed in a disordered pattern, which explains the irregular patterns that are observed during the shrinking-core process in Fig. 3. After all of the octahedral 16c sites are filled by Li, the rocksalt lattice becomes more isotropic to the incoming Li ions, which makes the subsequent conversion most likely to propagate across the outline of crystal, again as observed in Fig. 3.

**Discussion**

Given the basics of chemical thermodynamics, the equilibrium lithiation should go through the LiFe$_3$O$_4$ phase and the subsequent Fe + Li$_2$O composite in two non-overlapping processes, as proposed by Thackeray et al.$^{16–18}$. However, our in situ results show a clear overlap between the two steps, suggesting that the kinetic effects play an important role during lithiation. On the other hand, the phase-field theory, taking into account the effect of overpotentials, has succeeded in explaining the electrochemical kinetics in lithium-ion battery systems$^{53–55}$. We performed the phase-field simulation in the frame of non-equilibrium thermodynamics based on the Butler–Volmer equation$^{55,56}$ and the Cahn–Hilliard equation$^{23,57}$. To simulate the two-step reaction, we constructed a homogeneous free-energy function with three local minima corresponding to the pristine, intercalation and conversion phases, respectively. In addition, the kinetic contributions from overpotential and volumetric strain...
have also been included (details in Supplementary Methods). The calculated discharge voltage profile is shown in Fig. 5c, which qualitatively agrees with the experimental curves in Fig. 1e. Figure 5d shows the calculated lithium compositional profiles as a function of time (x-axis is the dimensionless lithiation direction and y-axis is the Li composition, details shown in Supplementary Movie 3). It is found that the formation of LiFe3O4 phase is predominant in the early stage of lithiation, whereas the conversion reaction initiates immediately afterward and propagates before the complete intercalation, resulting in a mixed lithiation behaviour, which is in good agreement with the in situ STEM observation (Fig. 3a). It is well-known that the lithiation process (redox stage and reaction speed) in a real battery is heterogeneous due to the fluctuation of local environments22. Here we reasonably assume that the local electrochemical conditions are identical for these two reactions within one nanoparticle. By comparing the in situ STEM results with phase-field simulation, we believe that the coexistence of Fe3O4, LiFe3O4, and Fe + Li2O phases are due to the competition between the intercalation and conversion reactions. The overall electrochemical kinetics dictates to the applied C-rate, which in turn determines the propagation speeds of the interfaces of Fe3O4/LiFe3O4 and LiFe3O4/Fe + Li2O. Although the reaction speed of intercalation is much faster, the conversion reaction accommodates more Li ions. Therefore, in terms of total lithium insertion capacity, both reactions give important contributions to the overall energy storage rate.

The kinetic lithiation mechanism we proposed here can accommodate the following phenomena which could not be interpreted by the equilibrium theory. (1) As for the discharge profiles in Fig. 1e and in literature9–11, even the intercalation reaction has not completed, the occurrence of conversion reaction on the surface will reduce the apparent discharge voltage, which consequently flattens the first plateau. (2) As for the previous debate on the existence of metallic Fe extrusion16–19, due to the kinetic effect, the conversion reaction can happen at the same time of the intercalation reaction, which induces the formation of metallic Fe. For the discharge process at a low rate, the extrusion of metallic Fe is not expected to be observed.

In summary, we have investigated the lithiation mechanism of spinel magnetite using an in situ strain-sensitive, BF-STEM technique, as well as DFT computation and phase-field simulation. By explicit visualization of the two-step intercalation-conversion process of the lithiation in Fe3O4 nanocrystals, we found that the initial lithium intercalation leads to formation of the rocksalt LiFe3O4 phase in a two-phase reaction mode, and the lithium intercalation process significantly overlaps with the subsequent conversion reaction within a single nanoparticle, leading to indistinctness of the discharge profiles. This scenario also clarifies the mechanism of metallic Fe extrusion during the intercalation process. Our findings have elucidated the ionic occupancy on the atomic level and revealed how rate-dependent kinetic effects can affect the reaction pathway at the single-particle scale. These findings highlight the importance of advanced in situ electron microscopy techniques in the field of lithium-ion batteries and provide valuable insights to improve the electrochemical performances of other spinel lithium metal oxide cathode materials.
Results

The in situ TEM TEM characterization was performed using a NanoFactory TEM STEM specimen holder, in which Fe3O4 nanoparticles dispersed onto a TEM half-grid with amorphous carbon support are analogous to the Fe3O4-C composite electrode, Li metal is coated onto a piezo-driven W probe as the counter electrode, with a thin layer of Li2O formed on Li metal as the negative electrode. A Celgard separator 2400 and 1 M LiPF6 electrolyte solution in 1:1 w/w ethylene carbonate/dimethyl carbonate were used to fabricate coin cells. Testing was performed on computer controlled systems (Arbin BT2000 and BioLogic VMP3) at 21 °C.

Electrochemical measurements. Composite electrodes were prepared with 80 wt% active material, 10 wt% polyvinylidene fluoride and 10 wt% acetylene black in NMP (N-methyl-2-pyrrolidone) and cast onto copper current collectors. 2032-type Fe3O4 nanoparticles were dispersed onto a TEM half-grid with amorphous carbon support are analogous to the Fe3O4-C composite electrode, Li metal is coated onto a piezo-driven W probe as the counter electrode, with a thin layer of Li2O formed on Li metal as the negative electrode. A Celgard separator 2400 and 1 M LiPF6 electrolyte solution in 1:1 w/w ethylene carbonate/dimethyl carbonate were used to fabricate coin cells. Testing was performed on computer controlled systems (Arbin BT2000 and BioLogic VMP3) at 21 °C.

Discussion

The authors then discuss the results of their experiments, focusing on the electrochemical properties of the Fe3O4 nanoparticles. They conclude that the nanoparticles show promising lithium storage capabilities, with high capacity and good stability.

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Author contributions
K.H., S.Z., D.S. and C.B.M. conceived and designed the experiments. K.H., S.Z., D.S. and J.L. performed in situ and ex situ TEM experiments. S.Z., H.Y. and C.B.M. synthesized the Fe3O4 samples. J.L., X.Y., E.H., X.-Q.Y., K.S. and H.G. conducted electrochemical tests. Yizhou Z. and Y.M. performed DFT calculations. Q.M. performed phase-field simulations. K.H. prepared the figures and wrote the manuscript with D.S., S.Z., E.A.S., Yimei Z. and C.B.M. supervised the project. All the authors participated in discussion of the results.

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