

Visualization of Phase Evolution of Ternary Spinel Transition Metal Oxides (CuFe₂O₄) during Lithiation

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Li-ion batteries (LIB) are under intense investigation because of their high energy density and power capacity. Among all candidates, nano-sized transition metal oxides (TMOs) provide incomparable electrochemical performance in terms of theoretical capacity and cycling [1,2]. Copper ferrite (CuFe₂O₄) has been considered as anode material for LIB due to its low toxicity, large abundance and high theoretical capacity (896mA/g). However, the symmetries of the crystal structure can vary, depending on the different cation occupancy in the tetragonal site (A-site) and octahedral site (B-site). A tetragonal CuFe₂O₄ (t-CuFe₂O₄) with disordered inverse spinel structure have all of Cu²⁺ atoms sharing octahedral sites with approximately half of the Fe³⁺, while the rest half of Fe³⁺ occupy the tetragonal sites. The phase evolution of TMOs with spinel structure, such as Fe₃O₄, during lithiation have been well reported [3]. However, the dynamic process of tetragonal CuFe₂O₄ during first discharge has not been fully understood yet. Since some phases that occur during reaction are meta-stable, it is critical to study the reaction as close as possible to that which would inside a real battery. Here we have used S/TEM, both *in-situ* and *ex-situ*, to directly visualize and characterize the reaction both morphologically and structurally.

In this work, we performed the *in-situ* STEM imaging to observe the structure evolution during the entire process in real space. Strain-sensitive bright-field STEM (BF-STEM) imaging is well-suited to detect small lattice changes in strain that occur during the intercalation reaction since this method collects signals from scattered electrons at a lower angle. Time sequenced BF-STEM images (Figure 1) illustrate the morphology evolution of particle A and B during lithiation. With Li-ions coming from the bottom, the darker contrast propagated from the bottom to the top, which represents the trajectory of intercalation. With further lithiation, clusters are initially formed at the bottom, as labeled in red dashed circle (at 422 s) indicating the extrusion reaction. At the final state (1009 s) clusters break into uniform fine-grained nanoparticles.

After visualizing morphology changes of t-CFO, we tracked the phase evolution through the entire lithiation process using *in-situ* electron diffraction as shown in Figure 2. The integrated intensity spectrum as a function of reaction time are plotted from series of SAED patterns (Figure 2a). The overall reaction is confirmed by the SAED pattern obtained from the pristine (Figure 2c) and final state (Figure 2b) which is $\text{CuFe}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Cu} + 2\text{Fe}^+ + 4\text{Li}_2\text{O}$. It corresponds with the electrochemical tests and *ex-situ* results. Moreover, Bragg angle changes correspond to the phase transformation through the reaction, such as the disappearance of t-CuFe₂O₄ (101) peak and formation of Li₂O (111) peak. It is worth noting that the t-CuFe₂O₄ (103) peak shows a left-shift in reciprocal space during the early stage of lithiation then it shifts to the peak indexed as Cu (111), which indicates the lattice distance expanded

at first then reduced.

References:

- [1] Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J.-M. *Ionics*. 2000, **6**, 321–330.
- [2] He, K.; Xin, H. L.; Zhao, K.; Yu, X.; Nordlund, D.; Weng, T.-C.; Li, J.; Jiang, Y.; Cadigan, C. A.; Richards, R. M.; et al. *Nano Lett.* 2015, **15**, 1437–1444.
- [3] He, K.; Zhang, S.; Li, J.; Yu, X.; Meng, Q.; Zhu, Y.; Hu, E.; Sun, K.; Yun, H.; Yang, X.-Q.; et al. *Nat. Commun.* 2016, **7**, 11441
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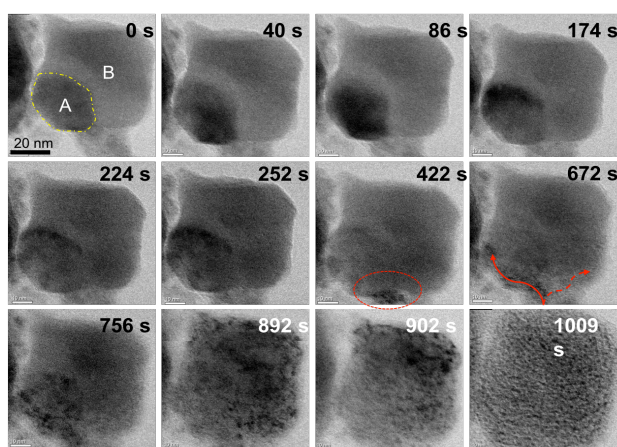


Figure 1. Time sequenced BF-STEM images show the phase evolution upon lithiation.

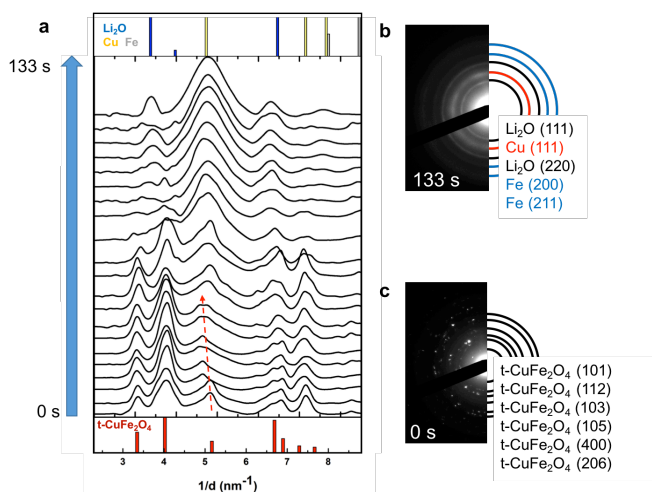


Figure 2. (a) Integrated intensity profile shows the phase evolution as a function of reaction time. (b) and (c) are the SAED patterns corresponding with integrated intensity profiles obtained in the fully lithiated state (133 s) and pristine state (0 s), respectively.