

Nanoscale Visualization and Intercalation in Many-Particle LiFePO₄ Electrodes

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The insertion and removal of lithium induce phase transformations in many lithium ion batteries. Understanding such phase transformations is essential to improving the charge rate and cycle life. Since its discovery in 1997 by Padhi, et. al., LiFePO₄ is one of the most studied phase transforming electrodes, yet its phase transformation mechanism remains unclear (1). Conventional diffraction and microscopy techniques cannot resolve the phase information at both the single particle and electrode levels, leading to great controversy and debate about the phase transformation pathways (2-5).

We used scanning transmission x-ray microscopy at the Advanced Light Source to image phase transformation at both the single particle and electrode length scales. By probing the oxidation state of iron at its L-edge, we can indirectly measure the distribution of lithium in an electrode at 25 nm resolution. We electrochemically cycled battery electrodes to different states of charges and imaged the distribution of lithium across several thousands of particles at different positions along the electrode. We have identified whether each particle is lithiated, delithiated, or phase transforming.

In this talk, we will present the phase transformation pathways spanning the individual and many-particle length scales. We find that the pathway is strongly dependent on the particle size and rate. During charge, LiFePO₄ transforms via a particle-by-particle pathway. During discharge, the particles transform concurrently, indicating a large asymmetry in the phase transformation. Additionally, the number of mixed particles appears proportional to the number of untransformed particles, suggesting a first-order relationship on the rate of transformation. We will also present a model which predicts the pathway across many parameter regimes.

References:

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