

## Analyzing Lithiation Dynamics in LiFePO<sub>4</sub> Cathode : Insights from TEM Experiments and Phase Field Modeling

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Lithium-ion batteries have revolutionized the field of portable electronics and electric vehicles by providing efficient and compact energy storage solutions. Despite advancements, several challenges continue to persist, such as limited battery lifespan, capacity degradation, and safety concerns. To address these issues and gain deeper insights into the underlying mechanisms, we present a comprehensive study involving an electrochemical liquid cell for in situ transmission electron microscopy (TEM) experiments. The utilization of the Dark Field technique (Figure 1) in this device enables us to directly observe the lithiation/delithiation process [1]. Through electron diffraction, we can track the modification of lattice parameters induced by the lithiation process.

In this study, we can observe the dynamic evolution of the delithiation interface between the LiFePO<sub>4</sub> (LFP) and FePO<sub>4</sub> (FP) phases inside a single crystal. This real-time monitoring provides valuable insights into the fundamental processes occurring during charge and discharge cycles. Additionally, we aim to evaluate the local displacement field extracted from the 4D-STEM ACOM (Acquisition of Crystal Orientation Maps) datasets [2-4]. Indeed, the lithiation process induces modifications in the lattice parameters of the FePO<sub>4</sub> host, necessitating the calculation of the symmetric strain tensor at the LFP/FP interface and the estimation of the elastic free energy density. By integrating 4D-STEM data treatments and analysis, we can accurately characterize the strain distribution and its influence on the phase transformation dynamics.

To gain a comprehensive understanding of the lithiation/delithiation dynamics and further elucidate the underlying mechanisms, we employ phase field model to simulate the diffusion phenomena. The phase-field model has proven to be a powerful tool for studying phase transformations and microstructure evolution in materials. Here, we use an Allen-Cahn type phase-field approach to investigate the phase transition from LiFePO<sub>4</sub> to FePO<sub>4</sub> cathode crystals in the presence of Li-ion chemical potential difference with the surrounding liquid electrolyte. The solid-solid phase boundary between LFP and FP phases modeled as a diffuse interface of finite width [5], and its motion is implicitly governed by the phase-field variable. We numerically solve a set of partial equations describing the temporal evolution of the phase-field variable and the chemical potential [6, 12]. By incorporating the real particle morphology, obtained by TEM imaging, and considering the smoothed boundary method (SBM) [10], our phase field model provides a more realistic representation of the lithiation/delithiation dynamics within LiFePO<sub>4</sub> crystals.

Initially, we employ a simple 2D model incorporating the chemical free energy and the interfacial free energy with a double-well potential approach [7]. By studying the kinetics of the lithiation/delithiation process within the LFP particle, which follows a one-dimensional Li-ion diffusion path, we observe two distinct regimes known as Surface Reaction Limited (SRL) and Bulk Diffusion Limited (BDL), as described in [8]. Our simulations are obtained by varying a kinetic parameter  $l$  in our equations, this parameter is inversely proportional to the net rate of insertion  $R$  that we find in [11].

Furthermore, we extend our model by incorporating the elastic free energy to consider its influence on the phase growth direction and shape during the LFP/FP phase transition [9] within a realistic LiFePO<sub>4</sub> single particle morphology. The elastic properties are adjusted using strain maps based on 4D-STEM data treatments and adaptative diffraction image registration.

In conclusion, this research explores the Li-ion insertion (or extraction) mechanisms into (or from) LiFePO<sub>4</sub> crystals using in situ TEM experiments combined with phase-field simulations. The correlation between the phase-field model and the 4D-STEM results provides valuable insights into the complex dynamics of phase transformations and microstructure evolution, contributing to the understanding of key factors affecting the performance and lifetime of Li-ion batteries. Our approach contributes to the elucidation of the intricate process that drives the dynamics of lithiation inside individual cathode materials during the electrochemical process.

### Graphic:

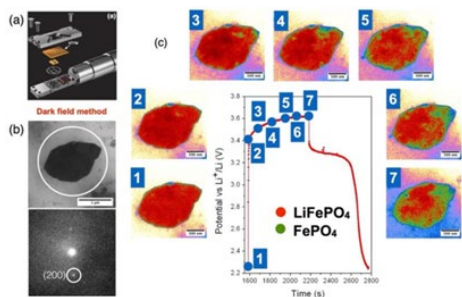


Figure 1: (a) In situ liquid electrochemical TEM cell. (b) TEM image of LFP single crystal surrounded by a liquid electrolyte. Electron diffraction pattern with (200) spot selected for the Dark Field imaging. (c) In situ monitoring of delithiation process in Li<sub>1-x</sub>FePO<sub>4</sub> using Dark Field image (TEM).

### Keywords:

Phase-field model, Allen-Cahn, LiFePO<sub>4</sub>, 4D-STEM

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