

Using Scanning Transmission X-ray Microscopy to Reveal the Origin of Lithium Compositional Spatiodynamics in Battery Materials

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Operando liquid cell microscopy has enabled the dynamic studies of electrochemical reactions in battery materials at the nano-scale and have started to produce relationships between battery performance and the structure and chemical composition of the battery materials. These fundamental relationships are critical to the development of next generation batteries. The initial liquid-electrochemistry microscopy studies were all conducted in the TEM [1-5]. Starting with work on open-cell systems using ionic liquids [1], which expanded work on *in-situ* TEM of solid-electrolyte materials, moving to closed-cell liquid TEM studies with battery electrode/electrolyte systems that are directly used in the current generation batteries. We have most recently expanded this approach to the X-ray synchrotron [6] and have been able to show fundamental mechanism underlying of ion insertion reactions at the solid-liquid interface at battery electrodes governing the rate capability and lifetime of Li-ion batteries.

We developed and used an *operando* scanning transmission x-ray microscopy (STXM) platform at Lawrence Berkeley National Lab's (LBL) Advanced Light Source (ALS) to map the dynamics of the Li composition and insertion/extraction rate in Li_xFePO_4 battery particles. Figure 1 shows the integrated liquid cell on X-ray beamline 11.0.2. We observed the structural changes between Li_xFePO_4 and FePO_4 of micron-sized particles as used in making electrodes for Li-ion batteries (Figure 2). These particles were dispersed on an x-ray transparent Pt electrode inside the liquid-electrochemical cell and were cycled at different (dis)charge rates while we acquired nanoscale x-ray absorption spectra at the Fe L3 edge with a 50 nm X-ray probe, which gave us the particle structure at any moment during cycling (Figure 2).

Using this *operando* microscopy approach we found that spatial variations in rate and in composition control the way lithium is inserted and extracted inside the Li_xFePO_4 battery particles. We varied the insertion and extraction rate constant between 0.2C and 2C to show that non-uniform domains are created. Spatial heterogeneities in reaction rates account for the domains, with the charging process significantly less uniform than the discharging process. The composition dependence of the rate constant amplifies heterogeneities during lithium extraction; however, it suppresses them during lithium insertion and at the same time stabilizes the solid solution. This coupling of lithium composition and reaction rates controls the kinetics and uniformity during ion insertion and extraction in the Li_xFePO_4 lattice [6]. These results highlight the important role of surface reaction rate for lithium insertion and extraction. Observing

inconsistencies of ion insertion and extraction have implications for battery electrode materials engineering for next-generation battery technology.

Looking ahead we will expand this study by conducting cross-correlative experiments in similar material systems across multiple microscopy platforms. The liquid-electrochemistry hardware developed for this work was already designed to perform these measurements between TEM, SEM and X-ray microscopes.

References:

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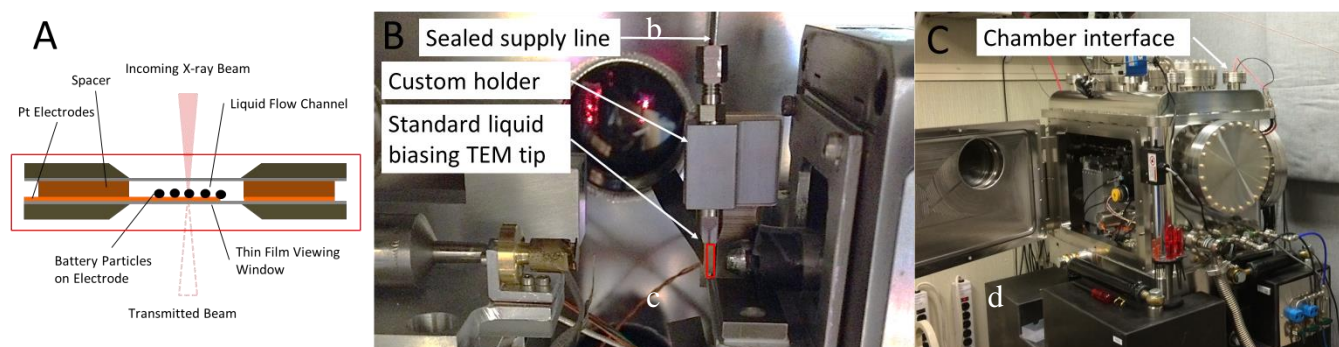


Figure 1. (A) Schematic of the assembled liquid cell. (B) Inside of the STXM chamber showing the liquid cell, supply line, and custom holder. (C) STXM beamline 11.0.2 at the ALS, LBNL.

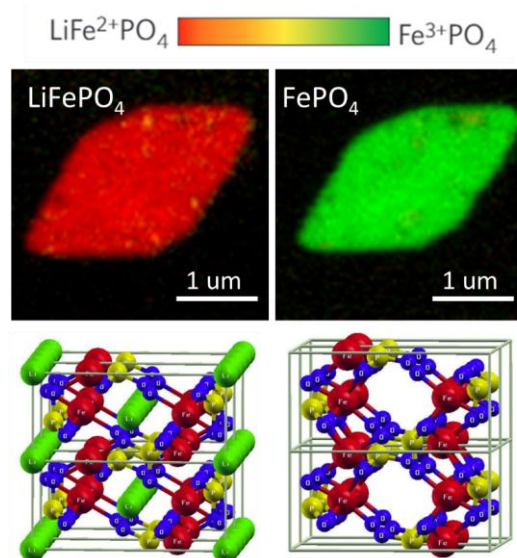


Figure 2. Operando state of charge maps as acquired from the STXM showing a charged (green) and discharged (red) Li-ion battery particle in the liquid-electrochemical cell.