2068
doi:10.1017/S1431927619011073

Microsc. Microanal. 25 (Suppl 2), 2019

Relationship between mechanical strain and chemical composition in $LiFePO_4$ via 4D-scanning transmission electron microscopy and scanning transmission X-ray microscopy

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Phase separation is an important factor for many Li-ion battery materials as it significantly impacts the capacity and cycle life of a battery. Forming Li-rich and Li-poor domains, phase separation induces changes to the composition and microstructure of these materials [1].

Scanning transmission X-ray microscopy (STXM) and X-ray ptychography are used to identify chemical composition changes in the Li-ion battery systems [2]. However, to understand the mechanisms of phase transformation, which effects the capacity loss and Li-insertion/desertion kinetics of the Li-ion battery systems, the relationship between Li-distribution and mechanical strain at phase separation interfaces must be delineated.

Four-dimensional scanning transmission electron microscopy (4D-STEM) uses a focused electron beam that is rastered across an electron transparent sample while a diffraction pattern is acquired at each scan position. Individual convergent beam electron diffraction (CBED) patterns provide comprehensive structural information, i.e., orientation, localized lattice strain, and other material properties [3]. These datasets, in combination with computational frameworks, enable high throughput analysis of localized lattice strain and ordering across micro-length scales.

Over thirty 4D-STEM datasets of $LiFePO_4$ particles at varying stages of delithiation ($LiFePO_4$, 50% delithiated $LiFePO_4$, and fully delithiated $FePO_4$) were acquired using a FEI Titan-class transmission electron microscope at an accelerating voltage of 300 kV. Maps of the infinitesimal strain matrix were produced using py4DSTEM, an open-source python based data analysis package, and contain ~5,000 CBED patterns each (Fig. 1) [4]. These maps show a clear variation in strain behavior as $LiFePO_4$ transforms via delithiation to $FePO_4$. Defined regions of compressive or tensile strain for the 50% delithiated particles is also observed. Segmentation into two distinct regions for the 50% delithiated $LiFePO_4$ strain map is expounded upon with position-averaged probability distributions of lattice vector lengths, *a* and *c*, in which bimodal distribution is apparent in the distribution of *a* for the 50% delithiated particle (Fig. 1g and 1h).

Using strain and lattice parameter data acquired by 4D-STEM (~2 nm resolution) with Li-distribution data acquired by STXM and X-ray ptychography (~10 nm resolution), a phase separation interface can be isolated and the chemo-mechanical relationship between strain and Li-distribution can be investigated for $LiFePO_4$ particles at varying stages of delithiation.

References:

[1] Holtz, M. et al., Nano Letters, **14**, (2014), pp.1453.
[2] Li, Y. et al., Advanced Materials, **27**, (2015), pp. 6591
[3] Ozdol, V.B. et al., Applied Physics Letters, **106**, (2015), pp.253107.
[4] https://github.com/bsavitzky/py4DSTEM. Code available under ‘copyleft’ GPL v3 license.
[5] This work was supported by the Toyota Research Institute through the Accelerated Materials Design and Discovery program. Work at the Molecular Foundry was also supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

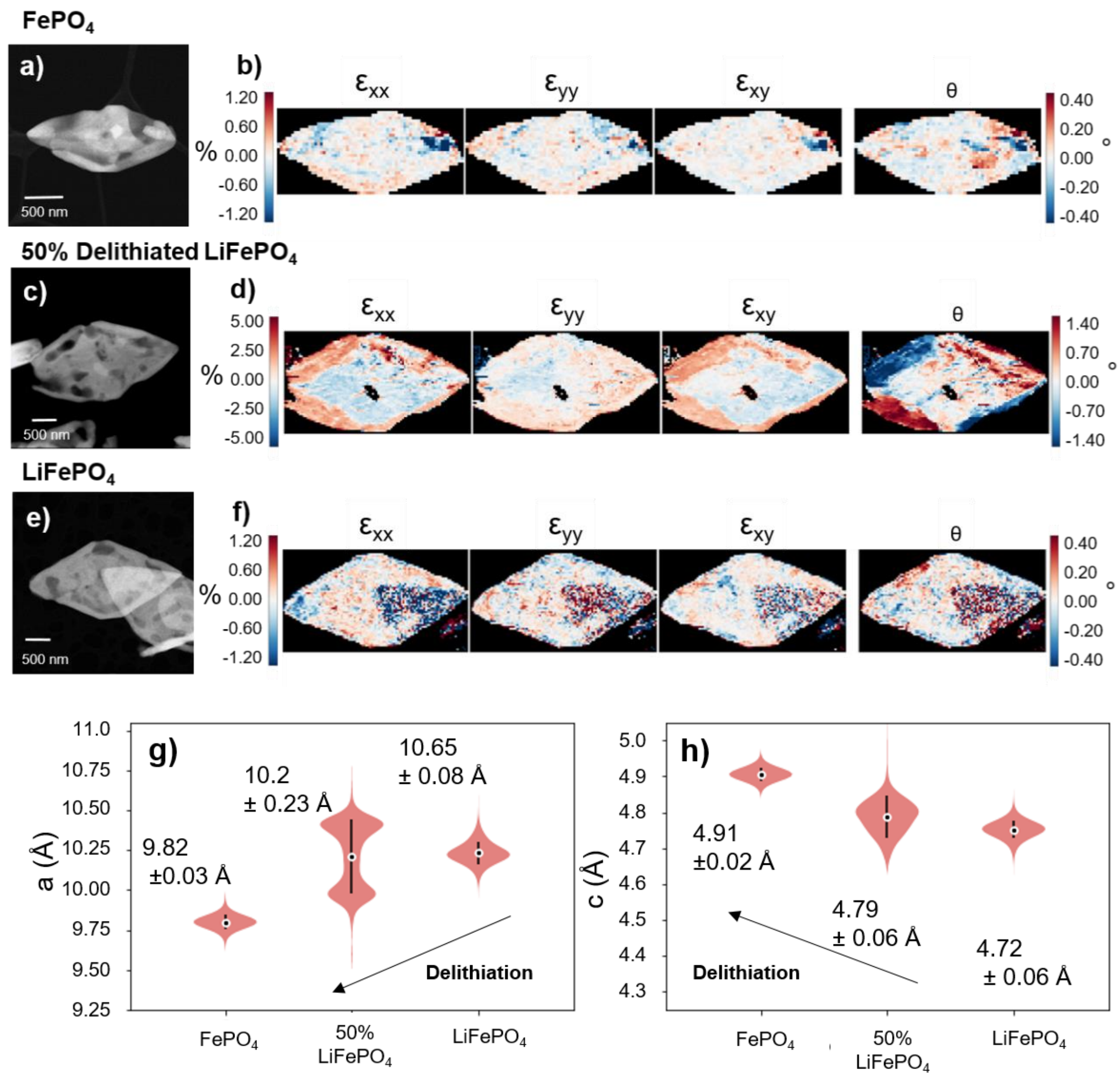

Figure 1. High angle annular dark field images of (a) $FePO_4$, (c) 50% delithiated $LiFePO_4$, and (e) $LiFePO_4$ particles. Infinitesimal strain matrix maps of (b) $FePO_4$, (d) 50% delithiated $LiFePO_4$, and (f) $LiFePO_4$ particles. Particles’ dimensions are approximately 2.0 x 4.0 x 0.3-0.5 μm. Violin plots detailing the mean and standard deviation of (g) *a* lattice parameter and (h) *c* lattice parameter for $LiFePO_4$ particles at varying stages of delithiation.