

# Non-equilibrium Pathways during Electrochemical Reactions in Battery Materials

## Scientific Achievement

Nanoscale *operando* visualization of the chemical and microstructural evolution of single crystal particles of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  on electrochemical cycling.

## Significance and Impact

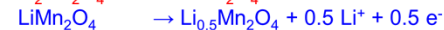
The existence of directional fracture and non-equilibrium reaction pathways identify limitations to performance that inform the engineering of optimized electrode morphologies and architectures.

## Research Details

- *Operando* full-field transmission X-ray microscopy was coupled with spectroscopy to follow the chemical and microstructural evolution in a technologically relevant Li-ion battery cathode.
- The onset and propagation of a series of complex phase transitions was visualized.
- Directional particle fracture, which causes degradation, was correlated to these transformations.

Work performed at U. Illinois, Chicago, UC San Diego and Santa Barbara, and SSRL and LBNL

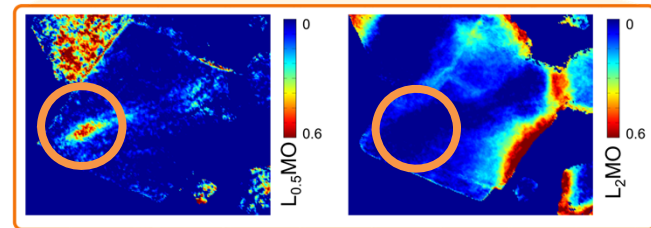
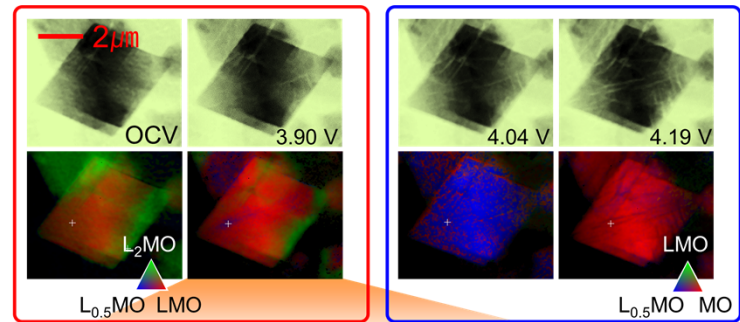
### Reactions observed:



$$E_1 = 2.9 \text{ V vs. Li}^+/\text{Li}^0$$

$$E_2 = 4.05 \text{ V vs. Li}^+/\text{Li}^0$$

$$E_3 = 4.15 \text{ V vs. Li}^+/\text{Li}^0$$



Spatio-chemical imaging of morphological changes (top row) and phase distribution (middle row) during electrochemical reactions from  $\text{Li}_2\text{Mn}_2\text{O}_4$  to  $\text{Mn}_2\text{O}_4$  (potentials indicated). Co-existence within the same single crystal particle of reduced ( $\text{L}_2\text{MnO}$ , right) and oxidized ( $\text{L}_{0.5}\text{MnO}$ , left) phases formed at potentials that are 1 V apart (circle in lower row).

Y.-S. Yu, C. Kim, Y. Liu, A. Van der Ven, Y. S. Meng, R. Kostecki, and J. Cabana, *Adv. Energy Mater.*, DOI: 10.1002/aenm.201402040 (2014).



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