

Operando Visualization of Two-Dimensional Li Diffusion Behavior and Hybrid Phase Transformation Kinetics in Olivine Lithium Iron Phosphate (LiFePO₄)

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Olivine lithium iron phosphate (LiFePO₄) is a technologically important electrode material for lithium-ion batteries and a model system for studying electrochemically-driven phase transformations. Despite extensive studies, many aspects of the phase transformation and Li transport in LiFePO₄ are still not well understood. Here we combine *operando* X-ray spectroscopic imaging and phase-field modelling to elucidate the delithiation dynamics of single-crystal LiFePO₄ microrods with long-axis along the [010] direction. Our study reveals two-dimensional Li diffusivity in microsized LiFePO₄ particles containing ~3% Li-Fe antisite defects and provides direct evidence for the previously predicted surface-reaction-limited phase boundary migration mechanism for the first time. Further, a new hybrid mode of phase growth is discovered, in which phase boundary movement is controlled by surface reaction or Li diffusion in different crystallographic directions. These findings uncover the rich phase transformation behaviours in LiFePO₄ and other phase-separating intercalation compounds in general and can help the design of better electrodes.

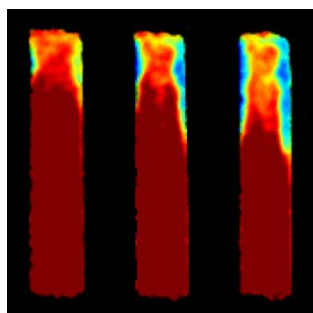


Figure 1 | Operando Visualization of Delithiation of LiFePO₄.

References:

[1] H. Liang*, L. Li*[‡], Y.K. Chen-Wiegart, J.J. Wang, K. Xiang, L. Gan, W.J. Li, F. Meng, J. Wang, Y.-M. Chiang, S. Jin, M. Tang, “Two-Dimensional Li Diffusivity and Hybrid Phase Transformation Kinetics in Olivine Lithium Iron Phosphate (LiFePO₄)”, *Nature Commun.* 2017, 8, 1194 (co-first and corresponding author)