

Interparticle Phase-Separation Dynamics in Dense Agglomerates of Lithium Iron Phosphate Nanoparticles

Bernardo Orvananos,¹ Hui-Chia Yu,¹ Rahul Malik,² Clare P. Grey,³ Gerbrand Ceder,² and Katsuyo Thornton¹

1. Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

2. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

3. Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK

Phase separation in olivine LiFePO_4 (LFP) has been observed in micron-size particles [1]. However, in practical application of rechargeable batteries, nano-sized particles are used in order to improve rate performances. Nano-sizing LFP particles can have a profound effect on its charge-discharge behavior. It can suppress the tendency for intraparticle phase-separation and instead lead to single-phase particles that are either at a Li-rich or a Li-poor phase [2], referred to as “interparticle phase-separation.” We have previously demonstrated the unique interparticle phase-separation dynamics of a dilute LFP nanoparticle agglomerate [3,4]. In this work, we focus on the interparticle phase-separation dynamics of a dense LFP-nanoparticle agglomerate. In this case, LFP nanoparticles are densely packed such that the particles are in contact with neighboring particles. Via the contact areas, Li can be directly transported between contacting particles without undergoing a redox reaction at the particle-electrolyte interfaces as in the case of dilute electrodes.

We have performed simulations assuming that Li can be transported across particle-particle interfaces. We also assume that particle-particle interfaces serve as potential phase boundary sites without interfacial energy penalty. (The existing particle-particle interfaces contribute to the free energy of the system, but we assume that it remains constant and independent of the Li concentration distribution.) Our simulation results show that the interparticle phase separation occurs for a greater range of rates than for dilute electrodes where particles are separated by the electrolyte. Since direct transport is not an electrochemical process, it occurs as long as the chemical potential of Li is different across the particle contact, facilitating phase separation even when the electrochemical driving force is absent. Furthermore, because the phase boundaries form at pre-existing particle contacts, phase separation is not inhibited by the interfacial energy penalty.

We thank Hao Liu and Aziz Abdellahi for their valuable comments. This work was supported as part of the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001294.

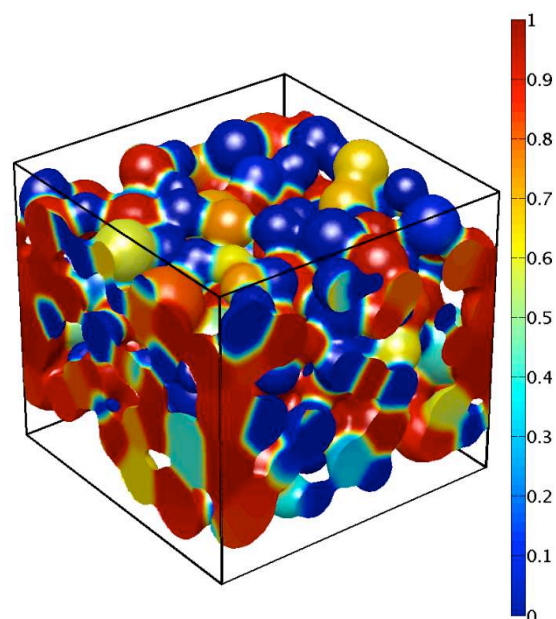


Figure 1: Connected agglomerate of 200 particles during the charge process at a 10 C-rate. The colorbar represents x in Li_xFePO_4

[1] G. Chen, X. Song, and T. Richardson. “Electron microscopy study of the LiFePO_4 to FePO_4 phase transition.” *Electrochemical and solid-state letters* 9, no. 6 (2006): A295-A298.

[2] W. Dreyer, J. Jamnik, C. Gohlke, R. Huth, J. Moškon, and M. Gaberšček. “The thermodynamic origin of hysteresis in insertion batteries.” *Nature materials* 9, no. 5 (2010): 448-453.

[3] B. Orvananos, H.-C. Yu, R. Malik, C. Grey, G. Ceder, and K. Thornton. “Simulations of Charge-Discharge Processes in an Intercalation Compound at the Nanoscale.” *Meeting Abstracts*. No. 629. The Electrochemical Society, 2012.

[4] B. Orvananos, H.-C. Yu, R. Malik, A. Abdellahi, C. Grey, G. Ceder, and K. Thornton. “A computational analysis of interparticle interactions in nano- LiFePO_4 electrodes.” *In preparation*