

Project

Phasefield modeling of Li-intercalation dynamics in $LiFePO_4$ -cathods for rechargeable Li-ion battery application.

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Project Description

$LiFePO_4$ is widely considered to be a promising cathode material for Li-ion rechargeable batteries. A number of nice properties such as low cost, safety, environmental friendliness, low toxicity, chemical stability, and its reasonable theoretical electrochemical capacity of 170 mAh/g, make it well-suited for large-scale battery application. State of the art understanding of the delithiation process in $LiFePO_4$, is

that it proceeds via first-order transformation processes, where a Li-rich phase transforms into an Li-poor one. However, there are a number of hints that multiple phases appear during the cycle, such as certain amorphous phases, solid solutions and discrete compounds [1].

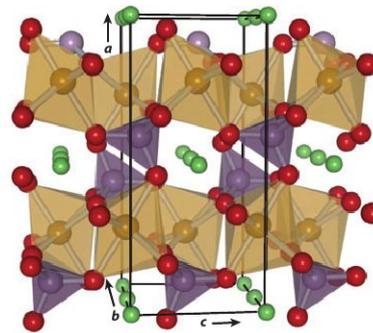


Figure 1: $LiFePO_4$ orthorhombic olivine structure exhibiting 1D Li diffusion channels along the b axis. The Fe octahedra are shown in tan, P tetrahedra in purple, Li atoms in green and O atoms in red. [1]

In order to shed light on the delithiation process in $LiFePO_4$ -cathods, we develop a continuum phase field model to describe the dynamics of Li-intercalation there. Within the phase field method moving phase boundaries, that occur between different phases, are treated as diffuse interfaces of finite width to avoid the necessity of explicitly tracking them. Then, this diffuse interface approach provides an elegant way to incorporate also the complicated effects that occur in these materials, such as the highly anisotropic ionic mobility of the Li-ions in the crystal, the electrochemical reactions at the phase boundary, stress and strain effects due to density differences between the phases, and so forth

[2]. Finally, this model at hand, we perform parameter studies, which provide insights into the sensitive interplay between the kinetics of phase transformations and the electrochemical transport of the Li-ions in the material.

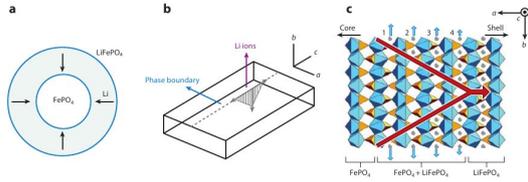


Figure 2: Schematics of several proposed growth models for the $LiFePO_4$ - $FePO_4$ phase transition. (a) Isotropic shrinking-core model Padhi et al., (b) Anisotropic growth model by Chen et al., (c) Anisotropic growth model by Laffont et al. [1]

Initial Simulations

The lithium intercalation process was simulated for a rectangular particle. A over-potential is applied to the top and the bottom of the system to provide driving force for Li insertion into an initially delithiated particle. The FP \rightarrow LFP phase transition occurs by nucleation in the particle corners being the most favored nucleation sites. A supercritical LFP nucleus was placed at the beginning of the simulation to initiate LFP growth. The progressive movement of the phase boundary was limited by diffusion. A steady state velocity is arising and a stationary interface profile is obtained. The shape of the front was caused by local lithium depletion.

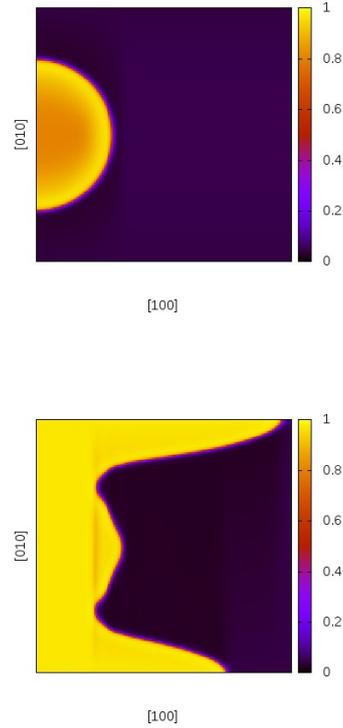


Figure 3: Particle discretized on a 200 x 200 mesh. The colours are representing the Li^+ concentration. Snapshots: start condition and during evolution.

References

- [1] Ming Tang, W. Craig Carter and Yet-Ming Chiang, , Annu. Rev. Mater. Res. 40:501-29, 2010.
- [2] G. K. Singh, G. Ceder and M. Z. Bazant, Electrochimica Acta, 53, 7599-7613, 2008.