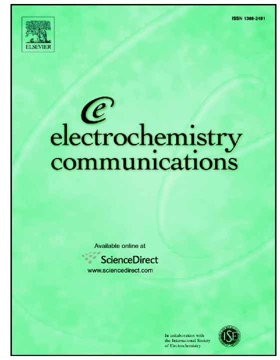
Size-dependent phase morphologies in LiFePO4 battery particles



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Size-dependent phase morphologies in $LiFePO_4$ battery particles

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Abstract

Lithium iron phosphate ($LiFePO_4$) is the prototypical two-phase battery material, whose complex patterns of lithium ion intercalation provide a testing ground for theories of electrochemical thermodynamics. Using a depth-averaged (a-b plane) phase-field model of coherent phase separation driven by Faradaic reactions, we reconcile conflicting experimental observations of diamond-like phase patterns in micron-sized platelets with observations of surface-controlled patterns in nanoparticles. Elastic analysis predicts this morphological transition for particles whose a-axis dimension exceeds the bulk elastic stripe period. We also simulate a rich variety of non-equilibrium patterns, influenced by size-dependent spinodal points and electro-autocatalytic control of thermodynamic stability.

Keywords: lithium iron phosphate, two-phase equilibrium, coherency strain, phase-field model, spinodal decomposition, electro-autocatalysis

1. Introduction

The morphology of two-phase coexistence in single crystals of the battery material $LiFePO_4$ has been the subject of much debate since its discovery over two decades ago [1]. Originally thought to be a low-rate material due the presence of phase boundaries separating $FePO_4$ and $LiFePO_4$, the material is now routinely used for high-rate applications [2]. At the same time, particle sizes have been reduced to the nanoscale, fueling interest in size-dependent and rate-dependent phase morphologies [3], which broadly affect intercalation-based electrochemical devices [4].

Such a dramatic reversal of fortune has drawn attention to this system as a model for studying the role of phase-separation in electrochemical systems, and spurred the development of sophisticated experimental techniques designed to image the phase state of single crystals. Observations of the morphology include stripes [5–8], lithiated cores [9–16], delithiated cores [17], both lithiated and delithiated cores [18], complex nonequilibrium morphologies [3, 19–22], and mosaic patterns of lithiated and delithiated particles (i.e. only single-phase particles) [3, 23, 24].

The reason why so many different morphologies occur in one system has remained a puzzle. Here, with the help of phase-field modeling, we show that elastic strain energy leads to significant morphological differences between nano and micro-sized particles. Whereas the equilibrium morphology of nanoparticles is controlled by elastic interaction between particle surfaces, that of microparticles is controlled by bulk elasticity. There is a stress-induced transition that depends on the size and aspect ratio of the particle, occurring around 250 nm for standard platelet $LiFePO_4$ particles, and the size-dependent nonequilibrium morphology is further influenced by driven intercalation reactions.

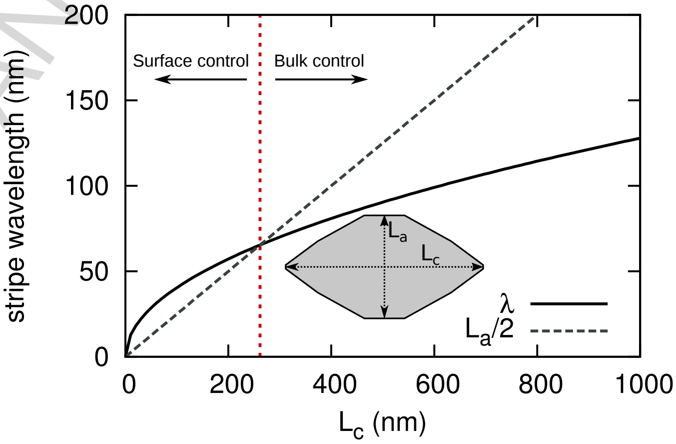

Figure 1: The transition from nano- to micro-phase morphology in $LiFePO_4$ platelet particles with aspect ratio $L_c/L_a = 2$ occurs at $L_c = 250$ nm. This is the point where the elastic stripe period λ (Eq. 1) exceeds $L_a/2$, half the particle size along its a-axis.

2. Theory

Previously, we showed that equilibrium phase separation in finite-size particles involves stripes, whose wavelength scales with the square root of particle size L_c along the c-axis [25]:

$$\lambda = \sqrt{\frac{2\gamma L_c}{\Delta f}} \qquad (1)$$

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