

Phase transformation kinetics and morphology in LiFePO₄

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Using a combination of first principles and phase field methods we investigated the phase front orientation of lithium-rich/lithium-poor phase boundaries as well as the charging rates achievable by nucleation and growth.

An analysis of the critical nucleus size and nucleation barriers as a function of the applied overpotential demonstrate that nucleation and growth cannot account for the high rates observed in LiFePO₄ electrodes even under a set of very generous assumptions. Nucleation rates at overpotentials below 150 mV were shown to be much too low to generate any observable phase transformation, whereas overpotentials as low as 50 mV are required in practice.

We will demonstrate that lithiation models which do not rely on the assumption of nucleation and growth may be better suited to assess the nature of the (de)lithiation mechanism of LiFePO₄ nano-particles. In particular, the non-equilibrium solid solution model provides an excellent alternative to nucleation and growth models. Through the existence of a non-equilibrium solid solution path accessible at low overpotentials, this framework has provided an explanation for the high rate capabilities of LiFePO₄ while being consistent with the two-phase bulk nature of this material.