

Stress-Induced Phase Boundary Instability and Its Effect on the Performance of Lithium Intercalation Compounds

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Ion-insertion-induced misfit stress due to lattice mismatch is common in intercalation compounds for energy storage applications and contributes to the mechanical degradation and capacity fading of batteries. In this work, we use theory and numerical simulation to demonstrate an important stress-diffusion coupling phenomenon during ion intercalation in electrode materials, in which the misfit stress triggers the morphological instability of the moving phase boundary between the lithiated and delithiated phases and results in non-uniform (de)intercalation kinetics. We propose that such a phenomenon can be generally observed in many battery compounds that undergo phase transformations upon cycling such as LiFePO_4 and $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{3/2})\text{O}_4$, etc. It could have important implications for battery performance and degradation, such as increasing the kinetic resistance to (de)intercalation and exacerbating stress concentration to cause fractures in electrode particles. Our analysis also suggests practical strategies to suppress this phenomenon, e.g. through the design of charge/discharge protocols with pulse currents and use of small particle size.

In the general theoretical treatment, we consider intercalation systems that undergo a first-order phase transformation with isotropic misfit strain and elasticity. The phase boundary between the Li-rich and Li-poor phases is assumed to be coherent. Analysis of the phase boundary migration kinetics reveal that the phase boundary is unstable against perturbations with wave wavelength above a critical value. Using typical values of elastic properties and interface energy for intercalation compounds, the fastest growing perturbation to the phase boundary is predicted to be in the range of 10 – 100 nm, which can readily develop in nano- and micro-sized particles. We find that the phase boundary is most susceptible to instability at the beginning and end stage of the (de)intercalation process, but can be suppressed in particles below a critical particle size. Therefore, nanoscaling electrodes not only benefits intercalation kinetics but also improves interface stability.

In addition to the theoretical analysis, phase-field simulations of the phase boundary evolution in LiFePO_4 and $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{3/2})\text{O}_4$ cathode particles are also performed. Consistent with the theoretical prediction, phase boundary instability is observed in both materials, which explains the observations of several recent synchrotron x-ray experiments.