Coupled mechanochemical theories for reacting systems with application to oxidation, nanovoid nucleation, and Li-ion batteries

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Hollow nanoparticles (NPs) are produced by void nucleation and growth during chemical reactions. However, there was no proper understanding of nucleation and growth mechanisms, and their predictive modeling. Furthermore, previous models based on the Kirkendall effect predicted the process time, which is larger by orders of magnitude than in the experiment. A continuum-mechanics approach for nucleation and growth of a nanovoid in reacting NPs based on the Kirkendall effect is developed, which quantitatively describes the experimental results for oxidation of copper NPs. The results show that the core is under compression (which eliminates fracture hypothesis), which promotes void nucleation by decreasing equilibrium concentration of vacancies at the void surface.

Si is a promising anode material for Li-ion batteries, since it absorbs large amounts of Li. However, insertion of Li leads to 334% of volumetric expansion, huge stresses, and fracture; it can be suppressed by utilizing nanoscale anode structures. Continuum approaches to stress relaxation in Li\textsubscript{x}Si, based on plasticity theory, are unrealistic, because the yield strength of Li\textsubscript{x}Si is much higher than the generated stresses. Here, we suggest that stress relaxation is due to anisotropic (tensorial) compositional straining that occurs during insertion-extraction at any deviatoric stresses. Developed theory describes well known experimental and atomistic simulation data. The stress evolution is modeled for different nanostructures (thin film, solid, and hollow nanoparticle) during lithiation-delithiation.

Oxidation is a coupled phenomenon that involves different physical processes—i.e., diffusion, chemical reaction, phase transformation, stress generation, and relaxation. Based on experimental studies, the growth strain is highly anisotropic and there is a lack of theoretical models to explain it. A general coupled large strain thermo-diffuso-chemo-mechanical model considering anisotropic inelastic (compositional and chemical) strain tensor is developed. A simple kinetic equation is derived to control the anisotropy of growth strain tensor, which connects the deviatoric stress to deviatoric deformation rate by only one constant. The oxidation of the aluminum substrate is modeled numerically and compared with experiment.