

# **Chemomechanics of lithium-ion battery anode particles:**

## **Role of geometry and surface effects**

Chemomechanics refers to a complex interplay of chemical and mechanical phenomena inducing and influencing each other in a coupled way. It is an integral part of the mathematical modelling of various multiphysics problems ranging over a plethora of applications, one among which is the interaction occurring inside the electrodes of a lithium-ion battery (LIB). The anode particles inside a LIB serve as an excellent platform to demonstrate the coupled interactions resulting from the chemical diffusion of lithium (Li) atoms and corresponding mechanical deformations of the anode particles. The urge for improved energy and power density with the growing need for portable energy-storage devices has driven the search for alternate anode materials that can replace the traditionally used graphite. Silicon, with a theoretical capacity ten times that of graphite, is the best replacement. However, it comes with an impending characteristic of huge volumetric expansion associated with Li insertion, and a subsequent contraction during Li dis-insertion. This frequent change in volume during each charging-discharging cycle leads to mechanical degradation, and eventual capacity fades. Strikingly, the usage of nanostructured anode particles meets this challenge considerably. But, as we venture into nano-dimensions, the surface-to-volume ratio increases, and surface stresses become significant. Surface stresses, not only modulates the stress magnitudes within the anode particles but also affect the overall performance of the anode particles. This study fundamentally addresses how the increasing significance of surface stresses at such lower dimensions, form an integral part in deciding the morphology and electro-chemo-mechanical performances of the anode particles used in Li-ion batteries.

The thesis primarily deals with four problems: first, an improved chemomechanical framework considering the dependence of the coefficient of compositional expansion on Li concentration, which is generally assumed to be constant; second, a finite deformation formulation for chemomechanical interactions within nano-structured, cylindrical Si anode particles considering surface stresses, and how the particle size and charging rate modulate the magnitude of the surface stresses; third, the influence of surface stresses on the mechanical and electrochemical performances of nano-structured, cylindrical Si anode particles under two different charging conditions: galvanostatic and potentiostatic; fourth, a generalized two-dimensional chemomechanical framework considering nano-holes within an infinite matrix, examining the influence of surface stresses on the morphology of these nano-holes, based on their sizes and proximity to the neighbouring holes.

Although the results and investigations are performed keeping in mind the lithiation/delithiation of Si anode particles, the proposed mathematical frameworks can be applied to other situations involving chemomechanical interactions. Further, these frameworks can be suitably modified to computationally analyse the behaviour of engineered materials before launching into costly manufacturing processes. These models can be extended to interpret other Multiphysics problems which are analogous to chemomechanical processes, like thermomechanical interactions, hydration-induced-swelling, etc.