Improvements in Chemo-Mechanical Modelling of Lithium-Ion Battery Anode Particles: Interfaces, Non-axisymmetric Growth, and Instability

Growing dependency on renewable energy and the surging use of portable electronic devices require the upgrade of commercially used lithium-ion batteries (LiB) to next-generation LiB, which can provide high capacity, high energy density, and long cycles. A major research thrust has been to investigate high-energy-density anode materials to develop next-generation LiB: chiefly, silicon, which undergoes alloying reactions during insertion of lithium (charging), referred to as lithiation. However, such an anode material faces significant challenges for commercial adoption as it experiences severe degradation during repeated charging and discharging. The degradation on the mechanical front can largely be attributed to the immense volumetric swelling together with the generation of stress referred to as diffusion-induced stress (DIS). The intricate mechanical and chemical events induce and enhance one another in a coupled way, and are referred to as chemo-mechanics. And, currently, massive efforts are on towards improving the modelling of such chemo-mechanical phenomenafor better mechanistic insights into lithiation.

This thesis has two overarching themes. *First,* improvements in chemo-mechanics associated with the first lithiation of crystalline silicon (c-Si), which is the most prevalent and affordable form of silicon available. We specifically concentrate on the phenomenon in which c-Si is lithiated to produce amorphous silicon (a-Si), which is followed by a reaction front between the lithiated and unlithiated phases (c-Si and a-Si). *Second,* exploring the various types of buckling and instability observed during the charging process by introducing a mathematical tool that can predict the critical values of a particular parameter responsible for that.

Under the aforementioned two themes, we address *four problems*: In the first problem, we formulate an improved chemo-mechanical framework for the first lithiation of c-Si, that lets us predict the velocity of the c-Si/a-Si interface, bringing a close match with experimental data available in the literature. In the second problem, we further improve the framework by incorporating an orientation-dependent interface reaction that can mimic experimentally-observed non-axisymmetric growth and facet evolution. Existing theoretical work in this area ignores stress-enhanced diffusion and the kinetics of addition reactions at the interface, which we duly take cognizance of. In the third problem, we apply the chemo-mechanical framework for first lithiation of c-Si to a buckling analysis. In the fourth problem, we change tack and develop a generalised framework for stability analysis employing the mechanics of incremental deformation. To the best of our knowledge, this is the first incremental deformation-based instability model in the context of chemo-mechanics that does *not* utilize the incompressibility condition for material behaviour. This model is posited to be a major improvement on extant Euler buckling type models which are hinged on *a priori* kinematical hypotheses.

A major portion of this thesis is invested in the significance of the first lithiation of c-Si, where diffusion-induced deformation takes place, and the material loses its stability. Therefore, we hope these models will contribute towards understanding the complex lithiation mechanism of c-Si, thereby contributing towards the commercial adoption of silicon as a next-generation anode material.