# Chemomechanics of Phase Transformation in Amorphous Silicon

Xavier Bruant*[1,2], Anh Tuan Le[3], Michel Rosso[4], Francois Ozanam[4], Michel Jabbour[3], and Laurent Guin†[3]

[1]Laboratoire de mécanique des solides – Ecole Polytechnique, Centre National de la Recherche Scientifique, Institut Polytechnique de Paris – France

[2]Laboratoire de physique de la matière condensée – Centre National de la Recherche Scientifique, Ecole Polytechnique – France

[3]Laboratoire de mécanique des solides – Ecole Polytechnique, Centre National de la Recherche Scientifique, Institut Polytechnique de Paris – France

[4]Laboratoire de physique de la matière condensée – Centre National de la Recherche Scientifique, Ecole Polytechnique – France

## Abstract

Silicon electrodes for lithium-ion batteries exhibit a theoretical capacity ten times higher than that of graphite electrodes currently used in commercial systems. When lithiated/delithiated, silicon experiences stresses on the order of 1 GPa, thus inducing damage in the material which results in poor cyclability and dissipation unfavorable to energy storage. These stresses affect the material from its very first lithiation, which proceeds through a phase transformation involving the progressive invasion of the pristine Si phase by an amorphous lithiated LixSi phase (1). Nonequilibrium continuum thermodynamics predicts that mechanical stresses affect the lithiation itself differently when the material is homogeneously lithiated (monophasic lithiation) than when it undergoes a phase transformation (biphasic lithiation) (2).

When monophasic lithiation takes place (without any phase transformation), mechanical stresses affect lithium insertion through the chemical potential of the diffusing species (Larché-Cahn theory). This coupling was first probed experimentally in homogeneous lithiation using a method whereby the stress state of silicon was modified indirectly through incremental delithiation (3). In contrast, in a first study we have investigated experimentally the coupling under homogeneous lithiation conditions by imposing an external mechanical loading on an amorphous silicon thin-film electrode at various lithiation rates and measuring its effect on the electrochemical response of the battery cell (4). This mechanical loading was applied by deforming elastically the steel substrate of the silicon thin film, which made it possible to directly probe the contribution of mechanics to the lithiation/delithiation processes. In this preliminary study, we showed that the instantaneous change in the electrochemical potential and its subsequent relaxation are well captured by a viscoplastic flow rule for the amorphous material, which could then be fitted to the data with good predictive capabilities. This material behavior law can then be used to model the phase transformation.

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*Speaker

†Corresponding author: laurent.guin@polytechnique.edu

In the present work, we concentrate on the effect of an external mechanical load on the phase transformation that occurs during the first lithiation, both experimentally and through modeling. Our experiments show that when undergoing a phase transformation, the very same external mechanical loading as that applied during homogeneous lithiation leads to a very different response of the silicon electrode potential. Under galvanostatic conditions and in the absence of any external mechanical load, the electric potential follows a plateau, indicating that the lithiation proceeds through a phase transformation. While the application of a strain increment on the thin film during this plateau results in an instantaneous change in potential similar to the one observed during homogeneous lithiation, the subsequent voltage relaxation displays a very distinct yet reproducible pattern, which we attribute to the interplay between stress evolution and phase-boundary kinetics.

To rationalize these observations, we resort to different modeling techniques aiming at describing the mechanisms underlying the phase boundary motion. First, an Arbitrary Lagrangian-Eulerian framework is developed to solve a sharp-interface model of the phase transformation in the one-dimensional setting of a thin film. This approach aims at describing the interactions between bulk rheological behaviour, chemical transport and phase boundary motion during the first lithiation. An implicit finite-element numerical implementation is formulated, and reaction-limited and diffusion-limited kinetic regimes are investigated.

This sharp-interface model is then employed to calibrate a phase-field model based on a grand-canonical formulation (5), which is more amenable to simulations of complex phase-front geometries. Such a model allows for a natural formulation of chemical equilibrium at the phase front while offering an independent degree of freedom for the phase-front kinetics, one which is not available in the popular Cahn-Hilliard models (6). In this sense, the proposed phase-field model is a mere numerical regularization of the sharp-interface model whose application is limited to the one-dimensional setting. The problem is formulated in a variational framework and numerical strategies are discussed.

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