

## **SEED PROJECT: MECHANICS OF ENERGY STORAGE MATERIALS**

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The goal of this new MRSEC seed project is to elucidate the fundamental interaction between solid mechanics and electrochemistry in advanced energy storage devices such as lithium ion batteries (LIB). Our current attention is focused on silicon, which is expected to be the anode material in the next generation of higher energy density LIB. Silicon is an attractive anode material because its theoretical charge capacity is an order of magnitude higher than that of graphite, which is the anode material in present day LIB. However, silicon undergoes large volume expansion (~ 400%) during charge-discharge cycling, which leads large stresses. These stresses have three broad consequences: (i) cracking and fragmentation of anode, which results in capacity fading and low cycle life of LIB (i.e. loss of reliability); (ii) energy dissipation in the anode due to plastic flow and lower energy recovery efficiency; (iii) interaction between stress and electrochemical parameters (anode potential, exchange current density at the electrode/electrolyte interface, maximum realizable charge capacity and diffusivity of Li), which influences the overall performance and efficiency of LIB.

These issues motivate a series of basic research problems at the interface between solid mechanics and electrochemistry, which are being investigated under this seed project. The specific questions on which progress has been made are: (i) Stress evolution in silicon thin film anodes during electrochemical cycling; and its influence on energy efficiency and reliability. (ii) Stress-diffusion coupling and its implications for charge-discharge kinetics. (iii) Experimental and computational characterization of mechanical properties of  $\text{Si}_x\text{-Li}_{1-x}$  alloys. (iv) Crack evolution and fragmentation in Si anodes. Progress on each of these issues is detailed below. Quantitative insights gained from the seed project are expected to contribute to the efforts to develop new anode materials and architectures for LIB.

This is a collaborative effort that involves experimental, analytical and computational components. This work is being carried out in close collaboration with scientists in the battery group at Lawrence Berkeley National Laboratory (LBNL). The scientific goals of this work are complemented by those of the General Motors/Brown Collaborative Research Center, which provides an industry perspective to identify the most relevant set of problems.

The broader theme of our work is to investigate the fundamental interactions between stress and chemistry in materials, which have important consequences in a variety of systems of technological importance such as batteries, fuel cells, hydrogen storage, catalysis and corrosion. This seed effort is a step towards these broader materials science challenges, which has practical implications for LIB. Significant advances in LIB technologies are crucial for current and future vehicular applications and for the emerging energy landscape in which intermittent sources such as wind, solar and wave are expected to play an increasingly significant role.

***Development of experimental facilities.*** In order to carry out the research outlined above, with MRSEC funding, a fully equipped experimental facility has been established at Brown by **Guduru** to simultaneously probe electrochemical and mechanical response of electrode materials. In preparation for this work, **Guduru** spent his sabbatical leave during 2008-09 at UC Berkeley, working with the battery group at LBNL. In the past few months, personnel from

LBNL battery group visited Brown and participated in some of the research activities described below). The experimental facility consists of a glove box with argon atmosphere, a multi-beam optical sensor (MOS) system for thin film stress measurement (integrated with the glove box); a micro-tensile test setup to simultaneously conduct electrochemical cycling and uniaxial loading on silicon thin films (designed and built in-house); a coin cell apparatus; an environmental chamber to test coin cells; an eight channel potentiostat; and custom electrochemical cells for simultaneous lithium electrochemistry and electrode stress measurement (designed and built in-house).

***Stress evolution in silicon thin film anodes during electrochemical cycling.*** Battery chemists have been experimenting with several different silicon anode configurations, such as pure Si micro- and nano-scale powders; Si dispersed in an inactive matrix; Si particles with different binders; Si micro and nano-wires; Si nanotubes; Si thin films, etc. This is an active area of research, with a large and rapidly evolving body of literature. However, very limited effort has been made to quantitatively understand the relation between stress evolution in Si and its state of charge. Moreover, almost all of the published literature on mechanical damage in Si anodes is qualitative and observational. In order to gain quantitative insights, **Guduru** conducted

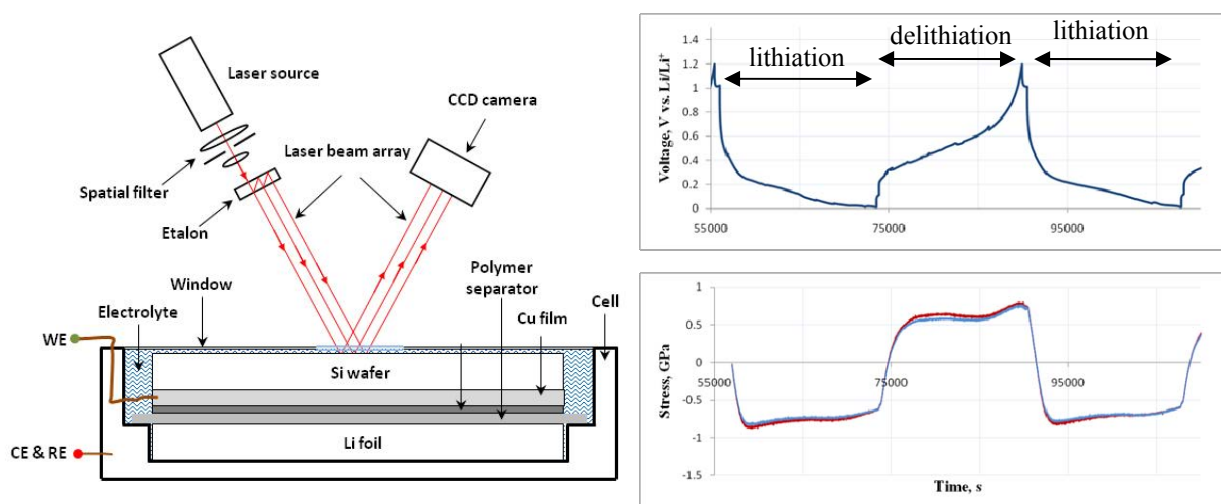


Figure 1. (left) Schematic illustration of an electrochemical cell with simultaneous stress measurement through MOS technique. (right) Cell voltage vs. time (top) and film stress vs. time (bottom) in a Si thin film sample deposited on a Cu layer.

experiments in which Si thin films were subjected to electrochemical charge-discharge cycling, while simultaneously measuring stress evolution in them. Stress measurements were made by monitoring the substrate curvature change by means of the Multi-beam Optical Sensor (MOS) method. A schematic illustration of the experimental setup is shown in Fig. 1, along with a sample plot of Si electrode potential vs. time (at a constant current of  $25 \mu\text{A}/\text{cm}^2$ ) and film stress vs. time. The main features of the experiments are: (i) As lithiation begins, the stress rapidly becomes compressive and the film reaches a state of compressive yielding. During subsequent lithiation, the film continues to flow plastically, while the flow stress drops slightly as lithiation proceeds. This is understandable if one assumes that the yield stress of the material decreases with an increase in Li concentration. (ii) When de-lithiation starts, the stress rapidly becomes

tensile and the film reaches a state of tensile yield. During subsequent de-lithiation, the tensile flow stress increases, consistent with the above explanation. Thus, the film alternates between compressive and tensile yielding during lithiation - delithiation cycles.

These measurements are useful (i) in quantitatively comparing the “mechanical merit” of different anode architectures; (ii) in calculating the driving force for crack propagation and damage accumulation in anodes; (iii) the data reveals that lithiated silicon, which is amorphous in these experiments, undergoes large scale plastic flow and dissipates mechanical energy; The mechanical dissipation can be calculated from the stress-time plots; it is estimated to be approximately 60% - 80% of the polarization losses in the cell. In other words, the experiments reveal that energy loss due to mechanical dissipation in a Si thin film electrode is comparable to that due to interface kinetics and ohmic resistance. The contribution of mechanical dissipation to the overall energy loss in a charge-discharge cycle has not been recognized by the battery community before, which highlights the importance of solid mechanics perspective in battery electrochemistry. Further, these results suggest that Si anode designs that minimize or eliminate plastic dissipation can significantly improve the energy efficiency of a Si anode battery. A more detailed experimental investigation is being pursued to address these issues.

In order to explore the influence of stress on the silicon electrode potential, we interrupted galvanostatic lithiation (or delithiation) as shown in Fig. 2, and the subsequent potential and stress relaxations were monitored. The relaxations of potential and stress, upon current interruption during lithiation, are represented by PQ and AB, respectively. Upon the resumption of the galvanostatic experiment, the electrode potential and stress rapidly return to the pre-interrupt state.

The potential and stress relaxations can be partly explained by the small concentration change associated with the relaxation of the double-layer, which drives both the electrolyte-reduction reaction, and the delithiation reaction (when the system is interrupted from the lithiation side, and vice versa). However, concentration change due to double-layer relaxation alone cannot explain the large stress drop and potential change. For example, from Fig. 2, if the stress drop during lithiation is attributed to concentration change alone, then the double layer would have to delithiate the electrode almost completely to the value at D. In which case, upon current resumption, it should have taken about 2 hours to return to the pre-interrupt state (*i.e.*, the duration for DA and SP). However, the pre-interrupt stress and potential states are regained rapidly in just a few minutes (BC and QR in Fig.

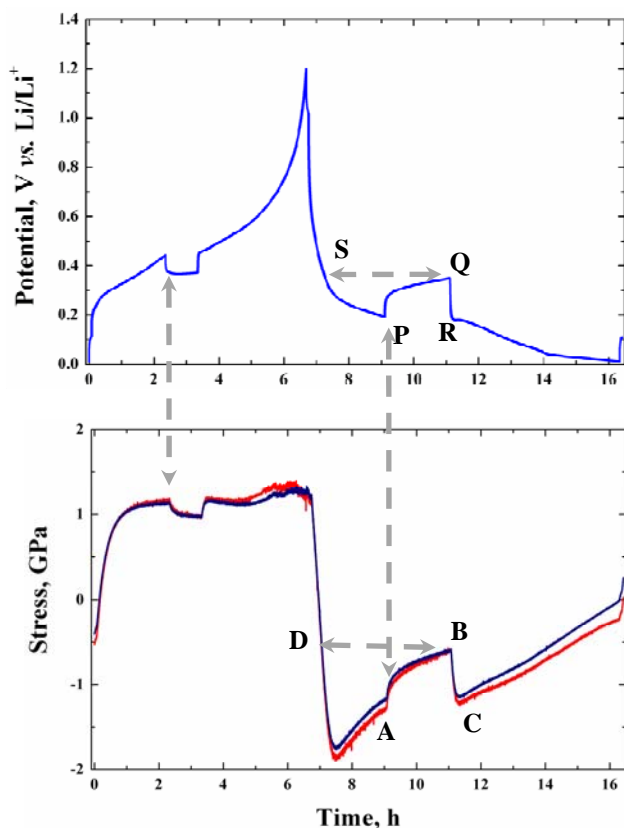


Figure 2. Transient cell potential (top) and film stress (bottom) upon open circuit relaxation. These experiments suggest that Si electrode potential is influenced by stress.

2). Hence, alternative mechanisms for stress and potential drop need to be sought. A potential explanation is that the drop in stress magnitude is driven by the viscoplastic relaxation mechanisms in the amorphous Si-Li alloy. Since the chemical potential of Li in Si is expected to have a significant contribution from stress, it is reasonable that the electrode potential also depends on stress. Further experiments are currently being pursued to characterize the dependence of electrode potential on stress by direct application of uniaxial stress on lithiated Si anodes.

Motivated by these experiments, **Bower** developed a model for lithiation induced stress evolution in Si thin films. The model is based on Larche and Cahn chemical potential for solid solutions and it explicitly considers the interface kinetics (Butler-Volmer equation), coupled stress-diffusion in the electrode and viscoplastic material response. The model predictions for potential vs. time and stress vs. time are shown in Fig. 3, along with the experimental results. The model captures all features of the experiments qualitatively. Further refinements to the model will be made to consider stress dependence of exchange current density and film cracking.

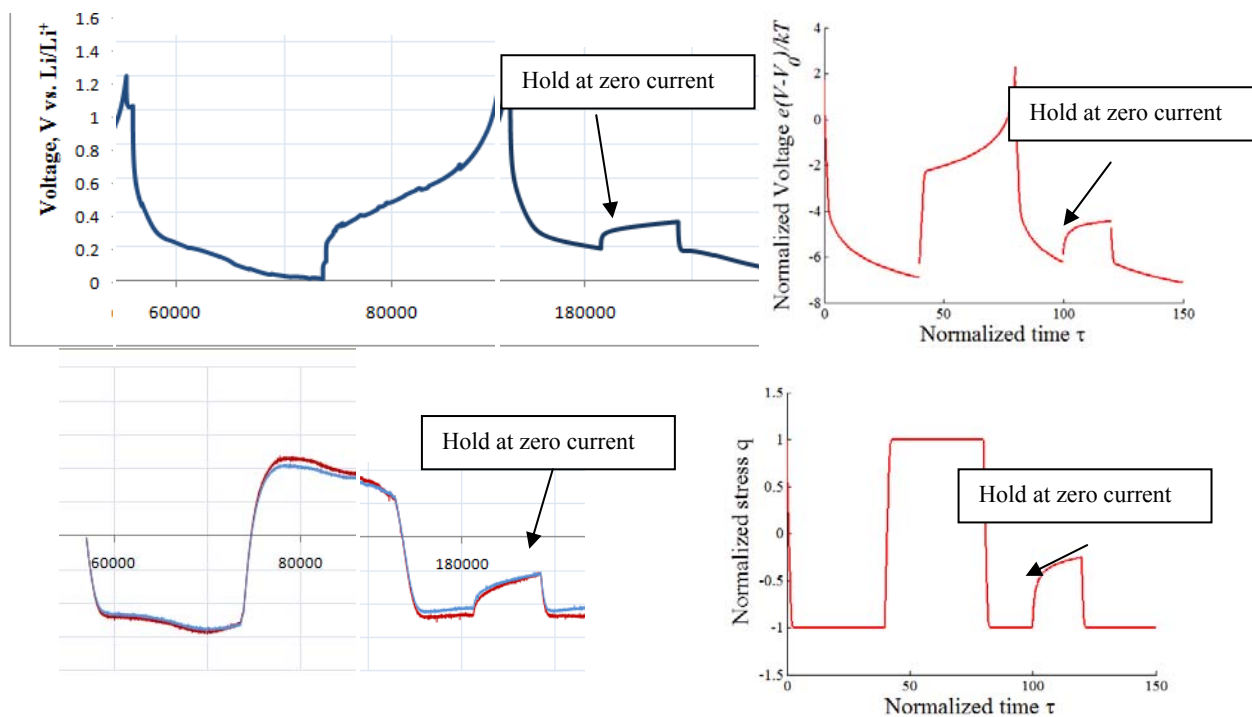


Figure 3. Comparison between experimental data (left) and model predictions (right) for electrode potential (top) and stress (bottom).

**Density functional theory (DFT) calculations of material properties of crystalline and amorphous Si-Li compounds:** Quantitative data on the mechanical behavior of Si anodes, i.e. their stress-strain behavior and fracture resistance, is essential in calculating the stresses generated in the anode, predicting the onset of cracking and driving force for crack propagation and de-bonding from the substrate. However, despite the importance of the mechanical behavior data of lithiated silicon, no such data is available in published literature; a thorough experimental and computational characterization of mechanical properties of Si-Li alloy is the goal of this task. It is well known that, after the first charge cycle, Si anodes lose their crystallinity and the

$\text{Si}_{1-x}\text{Li}_x$  alloy stays amorphous in the subsequent cycles. In the intermediate stages, some stable and metastable (for example  $\text{Li}_{15}\text{Si}_4$ ) crystalline structures are also observed, especially at high temperatures. **Shenoy** employed density functional theory based on the solution of Kohn-Sham equations to compute the elastic properties and electronic structure of LiSi alloys. A preliminary calculation of the bulk and Young's modulus of three crystalline LiSi phases are given in Fig. 4. Here, we first determined the array of elastic constants (3, 6 and 9 independent constants for the cubic ( $\text{Li}_{15}\text{Si}_4$ ), tetragonal (LiSi) and orthorhombic ( $\text{Li}_{12}\text{Si}_7$ )) and then used the Hill formalism to obtain the polycrystalline elastic moduli by performing an averaging over all crystalline orientations. Interestingly, the bulk modulus shows a linear decrease as a function of Li incorporation, while the Young's modulus does not follow this simple rule of mixtures. **Shenoy** also carried out electronic structure calculations to determine the band structure of the alloys. The preliminary work on crystalline compounds shows that LiSi is semiconducting with a band gap of 0.2 eV while the other phases are metallic. The relevant density of states calculations are shown in Fig. 5.

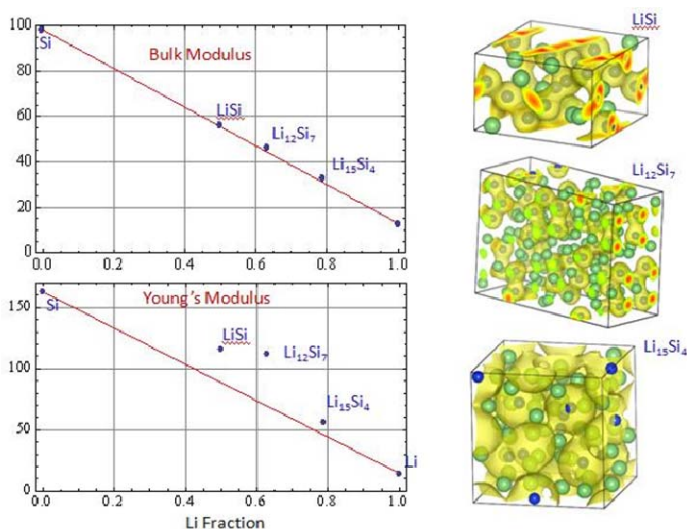


Figure 4. (Left) Hill averaged Bulk Modulus and Young's modulus of LiSi compounds computed using DFT. (Right) Electron charge density in LiSi compounds from DFT calculations. Note that in all cases electrons from Li are completely transferred to Si.

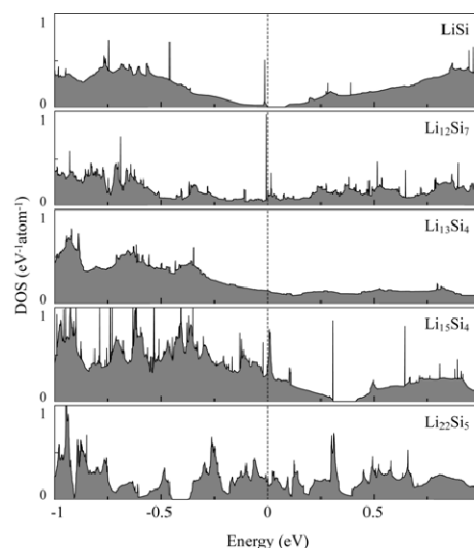


Figure 5: Density of states of different crystalline LISi alloys. LiSi is semiconducting with a band gap of 0.1 eV while the other alloys are conducting.

**Modeling crack nucleation under diffusion induced stresses in battery electrodes:** Li-alloy electrodes are known to suffer from pulverization, irreversible capacity and poor cyclability due to huge volume changes associated with the lithium ion insertion/extraction processes an example is shown in Fig. 6. Existing strategies to prevent decrepitation of Si have mainly focused on using composite materials and reducing the alloy particle size. In the latter approach, the emphasis is on reducing the size and experimenting with the geometry of electrode, where noticeable gains are observed in charge/discharge cycle performance and power density, compared to their bulk counterparts. Success of these experiments strongly suggests that size reduction is an effective strategy in creating fracture resistant, high capacity battery electrodes.

Motivated by such experimental observations, **Gao** developed a cohesive model of crack nucleation in an initially crack-free electrode subjected to *diffusion induced stress* (DIS)  $\sigma_I$

under galvanostatic (constant current  $i_n$ ) insertion and extraction processes (Fig. 7). Based on the magnitude of DIS compared to the cohesive strength  $S$ , the electrode material undergoes multiple or isolated strain localization leading to crack nucleation in the electrode. In our formulation, the elastic Green's function is used to establish an integral equation for traction along the cohesive zone. The criterion of crack nucleation is based on the maximum surface separation within the cohesive zone reaching a critical value which depends on the fracture energy of material. The presence of cohesive zone and its associated traction-separation law introduces a set of non-linear integral equations, for which the Newton-Raphson iteration scheme is implemented to obtain the solution. Furthermore, the spacing between the crack localization is determined based on the condition that stress in the electrode does not exceed the cohesive strength of material. Our analysis indicates that during both Li insertion and extraction, there exists a critical electrode dimension below which crack nucleation becomes impossible irrespective of the cohesive strength of the material. This critical length scale is identified to be on the order of

$$\ell_{ft} = \left\{ \Gamma(1-\nu)(FD)^2 / [E(1+\nu)(\Omega i_n)^2] \right\}^{1/3}$$

This suggests that the critical condition for crack nucleation in the electrode can be expressed as

$$i_n^{2/3} w = \text{critical}$$

Although the simple model adopted here brings out an appropriate length scale and the associated scaling laws, we plan to extend it for improved simulation and understanding of the decrepitation process in lithiated Silicon.

In related work, **Gao** and **Curtin** have studied diffusion during charging including various stress-dependent driving forces and stress-dependent diffusion activation barriers. The Ni-H system was used as a model system for which relevant material parameters needed in an analytic model could be determined from atomistic simulations and for which direct atomistic simulations could be performed for direct comparison to predictions of the analytic model. Given space limitations, details are not provided here but the study demonstrates that important interacting aspects of a variety of oft-neglected contributions to the overall diffusion process.

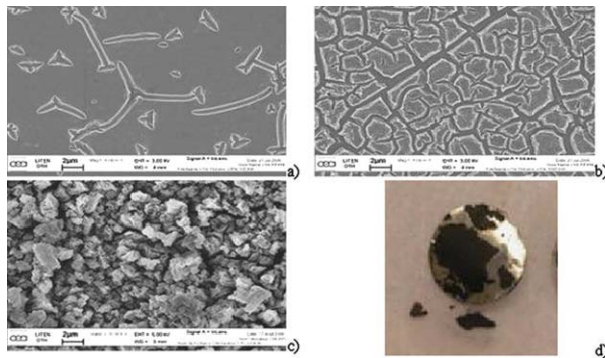


Fig. 6. SEM micrographs of germanium films after (a) 1, (b) 10, and (c) 110 discharge/charge cycles and optical micrograph of the sample after 300 cycles (Lafore et al., 2008).

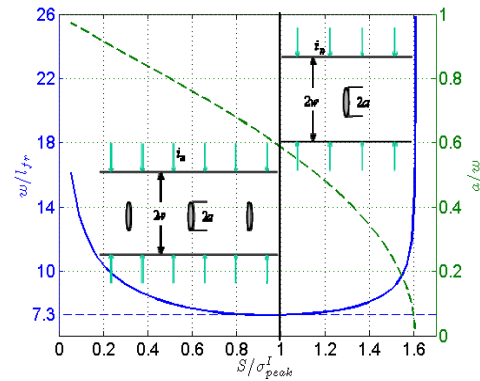


Fig. 7. Critical electrode half-width  $w$  and size of cohesive zone  $2a$  for nucleation of centre crack in an elastic strip electrode during galvanostatic Li insertion as a function of normalized cohesive strength.