

FINAL REPORT – covering period 7/1/2010-6/30/2012

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Recipient: President and Fellows of Harvard University

Project Title: *Hierarchical Petascale Simulation Framework for Stress Corrosion Cracking*

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Summary of earlier work:

In our earlier work we have demonstrated the feasibility of performing multiscale simulations using a coupling method appropriate for metals, which combines a small region treated by quantum mechanics within DFT and a much larger region treated classically by EAM potentials. We have also demonstrated that a careful treatment of residual stress in the classical region needs to be made in order to ensure that there are no spurious effects in the multiscale calculation.

With this theoretical basis, we were in a position to apply the method to the study of Ni embrittlement by S impurities at the grain boundaries, using a fully dynamical approach. This enabled us to address finite temperature effects and processes that may play a crucial role in the overall behavior of the system, such as amorphization and impurity segregation at the grain boundaries. Detailed studies of this nature constituted the next phase of the project, and provided new insight into the mechanisms of stress-corrosion cracking. These studies were a necessary complement to the simulations based on empirical potentials, such as the recently published work from the collaboration with the USC, and can serve as a validation of those results from a more fundamental perspective.

Work performed during final period

A) Multiscale modeling of Ni embrittlement by impurities

In continuation of our previous work, we completed the project on the multi-scale modeling of the embrittlement of Ni grain boundaries due to sulfur impurities. Specifically, we performed a first-principles DFT study of the mechanical behavior of fcc Ni in the presence of S impurities. The differences between bulk fcc Ni and fcc Ni with a $\Sigma 5(012)$ GB defect as S impurities are added were investigated. Low-energy interstitial positions for the S impurity atoms at the GB are the stable sites, versus the substitutional defect sites in the bulk fcc crystal. This already highlights the importance of GBs in chemical embrittlement and is consistent with the experimentally observed S segregation to GBs [1–9].

We employed Rice's theory to investigate changes in the ratio of the surface and the unstable stacking energy (the ductility parameter D) to quantify changes in the ductility. This approach was adapted to our system with a $\Sigma 5(012)$ GB by considering the competition between GB decohesion and shear in the form of GBS. GB decohesion, indicative of brittle behavior, is quantified through the work of separation (W_s), whilst GBS, a mechanism of plastic deformation in fcc metals, is quantified through γ_{us} , analogous

to previous work on GBs in crystalline solids [11–13]. By considering the energy of dislocation nucleation in the bulk and of GBS for our GB, in comparison with the decohesion energy and the work of separation, respectively, we are able to put this problem on a more complete and quantitative footing in the context of the competition between processes of cleavage and plastic deformation. Our calculations for the bulk defect-free structure indicate that an increase in ductility occurs as impurities are added. In contrast, we find that the resistance to shear, quantified by γ_{us} , increases for the GB structure. This limits plastic deformation and indicates a transition to brittle behavior, as this form of plastic deformation mechanism is removed. The effect of embrittlement persists when geometric factors are fully accounted for according to Rice's theory and when different combinations of slip and cleavage systems are considered. Although our results for the $\Sigma 5(012)$ GB show that GBS is suppressed with S impurity segregation, intergranular cracking facilitated by GBS in our simple geometric model does not become more preferred. We do not see the significant decrease of shear strength observed in MD calculations of amorphized GBs [10]; amorphization is important to enable easy intergranular crack propagation that is accommodated by GBS. Our results address the problem of a crystalline GB since analyzing an amorphous GB in the context of Rice's theory is not feasible. We show that even before any possible amorphization of the GB is considered, there is clear evidence for a significant decrease in ductility but not in the form of immediate intergranular fracture accommodated by GBS. This does not preclude intergranular fracture for large enough tensile forces, since the tensile strength decreases with the inclusion of S impurities. Any failure mode that relies on GBS is suppressed for the GB system.

This work was published in *Modeling and Simulation in Materials Science and Engineering* in 2012 (see list of Publications).

B) Lithium-Assisted Plastic Deformation of Silicon Electrodes in Lithium-Ion Batteries: A First-Principles Theoretical Study.

We subsequently turned our attention to the embrittlement and fracture of a very interesting system, that of the lithium-silicon alloy, that is being explored in the context of novel high-energy density batteries. Silicon can host a large amount of lithium, making it a promising electrode for high-capacity lithium-ion batteries. Recent experiments indicate that silicon experiences large plastic deformation upon Li absorption, which can significantly decrease the stresses induced by lithiation and thus mitigate fracture failure of electrodes. These issues become especially relevant in nanostructured electrodes with confined geometries. On the basis of first-principles calculations, we present a study of the microscopic deformation mechanism of lithiated silicon at relatively low Li concentration, which captures the onset of plasticity induced by lithiation. We find that lithium insertion leads to breaking of Si-Si bonds and formation of weaker bonds between neighboring Si and Li atoms, which results in a decrease in Young's modulus, a reduction in strength, and a brittle-to-ductile transition with increasing Li concentration. The microscopic mechanism of large plastic deformation is attributed to continuous lithium-assisted breaking and re-forming of Si-Si bonds and the creation of nanopores.

More specifically, we studied the effects of Li in both crystalline and amorphous Si, using first-principles calculations based on Density Functional Theory. Our main findings are as follows: first, Td interstitial positions are the lowest-energy sites for Li insertion into c-Si, and that when four Li atoms surround a single Si-Si bond the covalent bond readily breaks and the two Si dangling bonds are essentially saturated by the formation of weak bonds of mixed ionic-covalent character with the nearby Li atoms. This is illustrated in Figure 1. Also, in a-Si with sufficiently high Li concentration (roughly $f =$

0.125 or higher) the structure undergoes a brittle-to-ductile transition with significantly lower Young's modulus, and plastic deformation becomes relatively easy. The essence of these results is that the chemical interactions of lithiation give rise to pronounced effects on the mechanical behavior of silicon structures. In particular, as the stresses induced by lithiation are limited by the yield strength, the fracture failure of the silicon electrode can be largely remediated by taking advantage of the plasticity of lithiated silicon. At the microscopic scale, we have identified and described by specific examples the atomistic mechanism responsible for plastic deformation (see Figure 1), which consists of continuous Si-Si bond breaking and reformation in the presence of Li. The plastic deformation of solid-like amorphous network in the vicinity of the glass transition point has been attributed to the thermally activated shear transformations around free volume regions, which bears some similarity to the atomic-scale deformations we have described for lithiated a-Si. In this project we have demonstrated that lithium-assisted bond breaking and re-forming is the mechanism responsible for plastic flow in amorphous silicon at low temperature under strain.

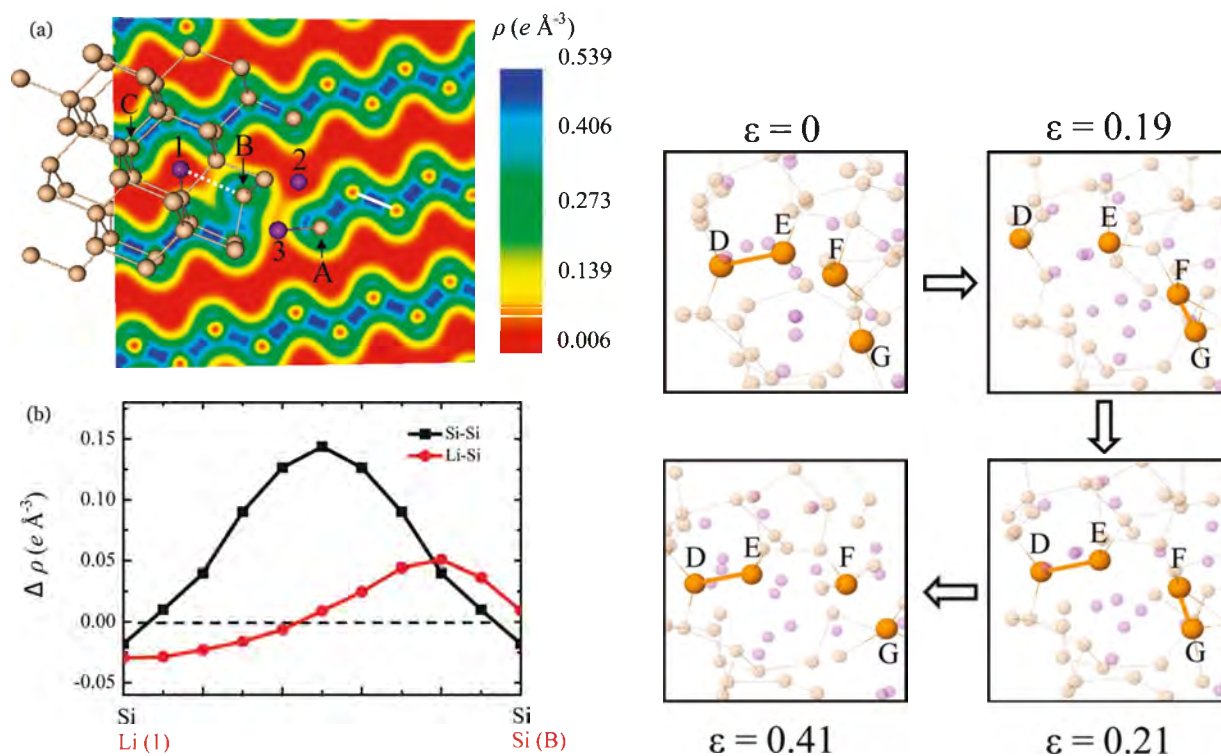


Figure 1. (a) Valence electron charge density distribution on a (110) plane in the lowest-energy configuration of c-Si with four Li atoms. (b) The charge density difference distribution along a Si-Si bond in pure c-Si represented by a solid white line in (a), and the Li-Si bond 1_B represented by a dashed white line in (a). The four panels on the right side illustrates a particular microscopic sequence of Si-Si bond breaking and reformation of lithiated silicon at Li concentration $f = 0.50$. The four snapshots correspond to the states of various strain values ϵ , as indicated. The two Si atom pairs D_E and F_G that undergo bonding/nonbonding/bonding and nonbonding/bonding/nonbonding transitions are enlarged for better contrast.

This work was published in NanoLetters in 2011 (see list of Publications).

C) Reactive Flow in Silicon Electrodes Assisted by the Insertion of Lithium

The success of the previous study led us to investigate further the process of embrittlement of the

lithiated silicon anode materials. In the search for high-energy density materials for Li-ion batteries, silicon has emerged as a promising candidate for anodes due to its ability to absorb a large number of Li atoms. Lithiation of Si leads to large deformation and concurrent changes in its mechanical properties, from a brittle material in its pure form to a material that can sustain large inelastic deformation in the lithiated form. These remarkable changes in behavior pose a challenge to theoretical treatment of the material properties. Here, we provide a detailed picture of the origin of changes in the mechanical properties, based on first-principles calculations of the atomic-scale structural and electronic properties in a model amorphous silicon (a-Si) structure. We regard the reactive flow of lithiated silicon as a nonequilibrium process consisting of concurrent Li insertion driven by unbalanced chemical potential and flow driven by deviatoric stress. The reaction enables the material to flow at a lower level of stress. Our theoretical model is in excellent quantitative agreement with experimental measurements of lithiation-induced stress on a Si thin film.

Specifically, we studied the microscopic mechanism of inelastic deformation of a-Si electrodes and stresses accompanying the lithiation reaction, using first-principles calculations based on density functional theory. We described the concurrent process of the Li insertion reaction and flow of lithiated silicon. We note that reactive flow of solids is observed in many other physical systems, but its theoretical treatment is largely undeveloped. Lithiation of silicon provides a useful model system to study the interplay of local chemical reactions and macroscopic mechanical deformation. The essence of the results in this paper is that the chemical reaction promotes mechanical flow, enabling a material to flow at a lower level of stress. We proposed a phenomenological model to describe the reactive flow of lithiated silicon and examined in detail the local atomic structures (see Figure 2) and electronic properties to elucidate the origin of the macroscopic mechanical behavior. The agreement between our theoretical treatment and experimental measurement is quite remarkable (see Figure 3), despite the limitations of the atomistic model which come chiefly from the size of the periodic supercell used to represent the amorphous Si material.

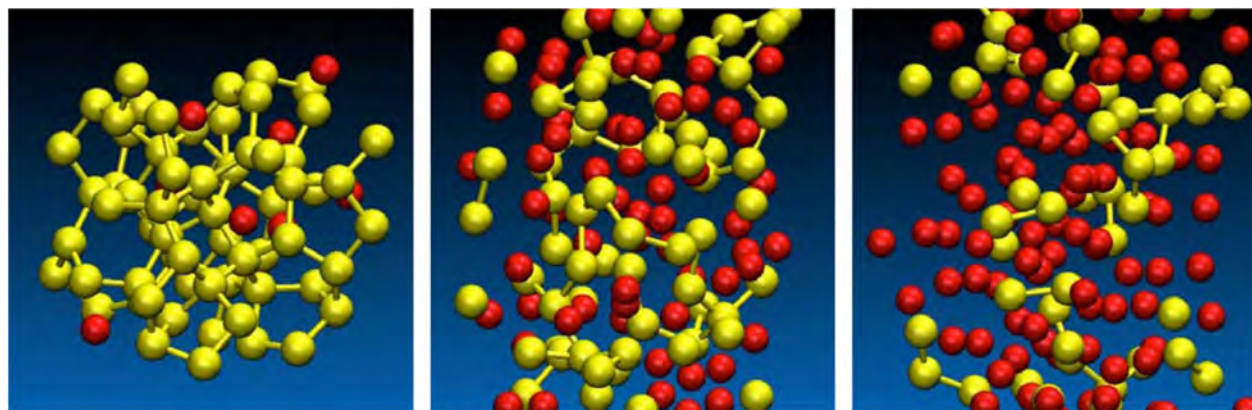


Figure 2. Examples of atomic-scale structure at different Li concentrations: $x = 0.125$ ($\text{Li}_8\text{Si}_{64}$, left panel), 1.0 ($\text{Li}_{64}\text{Si}_{64}$, central panel), and 2.0 ($\text{Li}_{128}\text{Si}_{64}$, right panel). Yellow spheres represent Si atoms, and red spheres represent Li atoms.

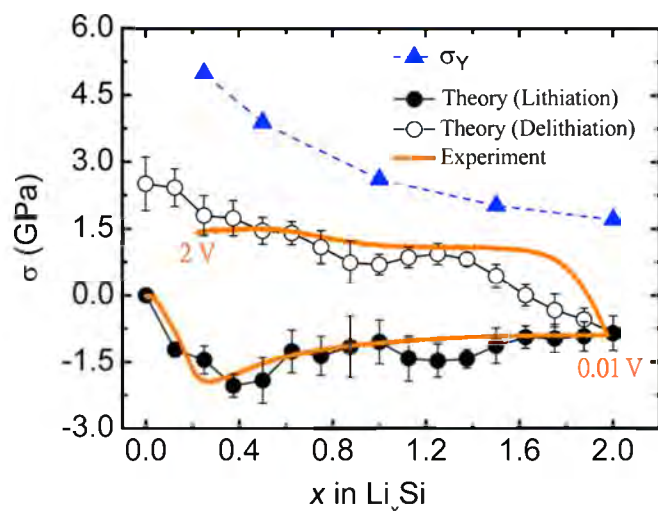


Figure 3. Evolution of the biaxial stress in an a-Si thin film electrode during a lithiation and delithiation cycle: The orange line shows the in situ measurement of the biaxial stress in the first lithiation cycle by the wafer curvature method. The electrode is cycled at 1C rate between 2 and 0.01 V vs Li/Li+. The black lines with symbols (filled for lithiation, open for delithiation) show the evolution of the biaxial stress in an a-Si thin film electrode during a lithiation and delithiation cycle based on first-principles calculations. The error bars represent standard deviations obtained from several configurations at each Li concentration. The yield strength of lithiated Si at a given Li concentration, obtained by uniaxial tension simulations, is shown by triangles.

This work was published in NanoLetters in 2012 (see list of Publications).

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(asterisks identify persons supported by the grant)

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