

## **Blue Waters Technical Report**

Project Title: **Mechanics of Deformation in High Capacity Lithium-Ion Batteries**

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### **Executive Summary**

Silicon is one of the most promising electrode materials for high performance lithium ion batteries, since it has an order of magnitude higher specific capacity compared to conventional graphite electrodes. However, Si electrodes crack massively during lithium insertion since they expand by 300% when fully-lithiated; they also delaminate from the current collector after a number of charge cycles. We have conduct massively parallel molecular dynamics (MD) simulations and density functional theory (DFT) calculations in Blue Waters (BW) to uncover the underlying mechanisms for cracking and delamination of the Si electrode during charge cycling; these mechanisms are in excellent agreement with experiments. BW resources were especially needed because of the computational scale of the problem and the large number of computational runs to cover the entire parameter space. Our results have provided rich insights into the design and engineering of damage tolerant electrode materials for high-capacity lithium ion batteries.

## Description of Research Activities and Results

### 1. Background and Motivation

Lithium ion batteries are high energy density systems that store energy by insertion of lithium ions into solid electrodes. Silicon is one of the most promising electrode materials for high performance lithium ion batteries, since it possesses the highest known specific capacity of 4200 mAh/g, which is an order of magnitude higher than conventional graphite electrodes. During lithiation, the silicon electrodes form  $\text{Li}_x\text{Si}$  compounds, and undergo huge volume expansion of about 300% since one silicon atom can theoretically bond with a maximum of  $x = 3.75$  lithium atoms. When attached to a metal current collector, such as copper, the massive and inhomogeneous volume changes during repeated lithiation and delithiation charge cycles lead to colossal cracking of the silicon electrode. Recent studies have shown that silicon electrodes of small feature sizes, such as nanowires, nanoparticles, porous structures, and thin films, display significantly higher reversible charge capacities and longer cycle life. In fact, a critical feature size of these nanostructured silicon electrodes exists, below which fracture would be completely mitigated. It is believed that the improved fracture resistance originates from the ability of the nanoscale structure to accommodate the lithiation-induced strain by plastic deformation, resulting in lower stresses present during volume changes. However, the delamination of crack-free nanostructured silicon electrodes from current collectors after a critical number of charge cycles has been widely reported, resulting in the loss of electrical contact and consequent capacity fade. Our research focuses on answering the following questions:

- What gives rise to the size-dependent cracking of lithiated silicon?
- Why does the lithiated silicon thin film electrodes delaminate from the current collector after a critical number of charge cycles?
- Why does lithiated silicon undergo plastic deformation, given that pure silicon is inherently brittle?

*Blue Waters resource justification:* To our knowledge, detailed analyses of both the plasticity and fracture process underlying lithiated silicon electrodes are virtually non-existent due to the computational complexity of such systems. Firstly, the lithiated silicon structures are amorphous. Recreating these structures requires substantial intermixing between lithium and silicon atoms through a heating and quenching process in molecular dynamics (MD) simulations and density functional theory (DFT) calculations which is computationally expensive. Secondly, elucidating

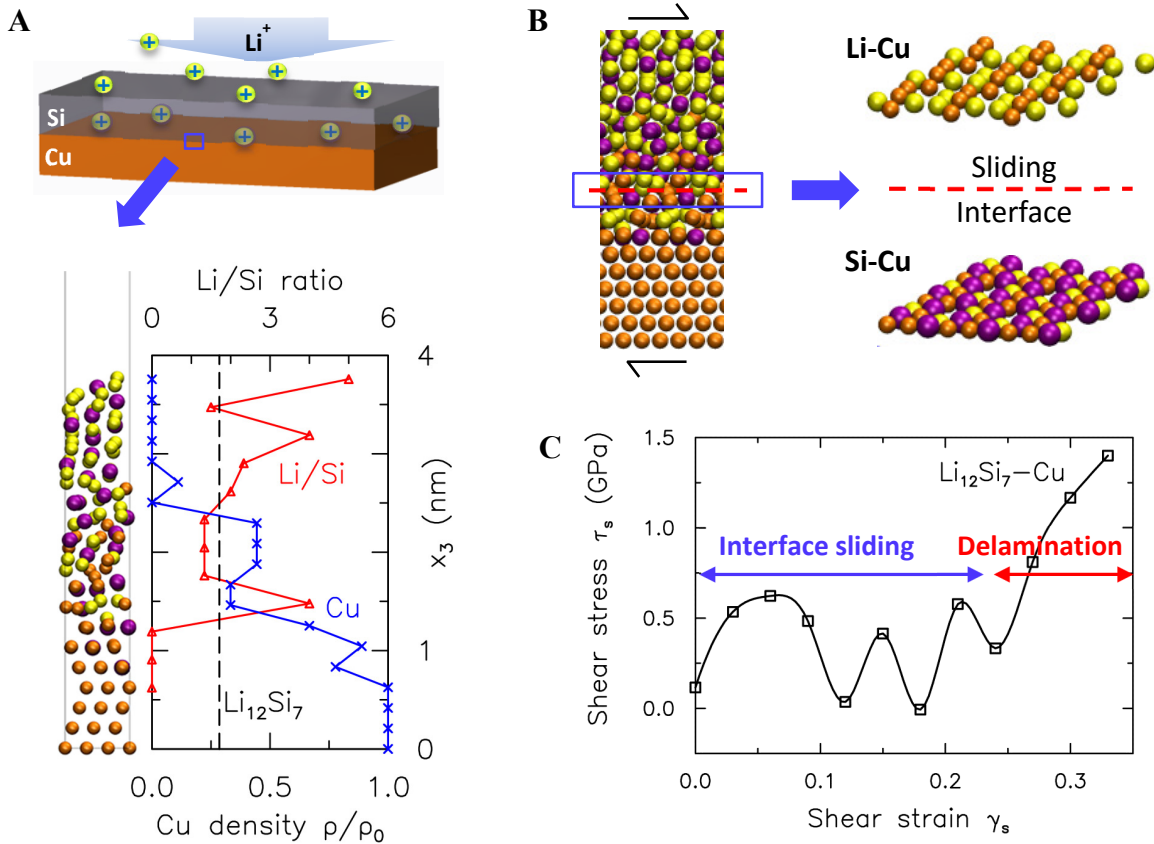
the plasticity mechanisms of lithiated silicon involves subjecting the representative unit cell in DFT to tensile loading, which has to be performed gradually in 1 to 2% load increments, followed by quantum-mechanical relaxation after each increment. One has to carry this out for structures with different Li:Si atom ratios. The computational complexity coupled with the large number of computational runs makes this a problem which requires the unique resources of Blue Waters (BW). The proposed DFT calculations and MD simulations will be performed on the research codes VASP and LAMMPS respectively. These codes are highly scalable and have been compiled and tested on BW.

## 2. Accomplishments

### 2.1 Sliding and delamination of a $\text{Li}_x\text{Si}$ thin film electrode from a Cu current collector

Even though the cracking of  $\text{Li}_x\text{Si}$  thin films can be mitigated through patterning individual silicon islands, the uncracked electrode still delaminates from the current collector after a critical number of charge cycles. To date, much is still unknown about the interface bonding the silicon electrode and a metal current collector, such as copper. Studies have suggested that sliding readily occurs along the silicon-copper interface to accommodate the massive volume changes in lithiated silicon during charge cycling. However, understanding the mechanisms of interface sliding and delamination is complicated by significant intermixing of Cu, Si, and Li atoms at the interface between a lithiated-silicon film and the copper substrate.

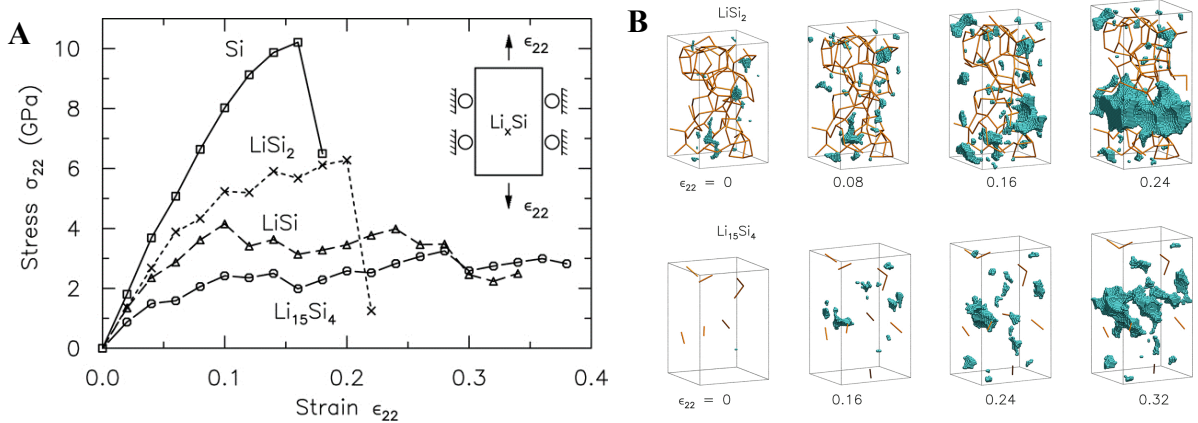
Using first principle calculations, we recreate model structures of the interdiffused Li-Si-Cu interphase (**Fig. 1A**), and show that the interdiffusion among Li, Si, and Cu atoms leads to the formation of well-delineated, crystalline Si-Cu and Li-Cu atomic layers at intermediate lithium concentrations (**Fig. 1B**). These atomic layers are weakly bonded in shear, and readily slide to relieve the interfacial stresses during lithiation processes. Ideally, interface sliding between the silicon electrode and the copper current collector will help limit film stresses introduced by the lithiation process. However, sliding between the Si-Cu and Li-Cu atomic layers cannot occur indefinitely. The formation of pinning defects in the form of  $\text{LiSi}_3$  compounds along the interface can eventually inhibit sliding (**Fig. 1C**). The consequential buildup of interfacial stresses leads to delamination failure of the silicon electrode from the copper current collector. Understanding the atomic-scale mechanisms that promote or impede sliding provides the critical first steps toward designing silicon-copper interface structures to mitigate electrode failure.



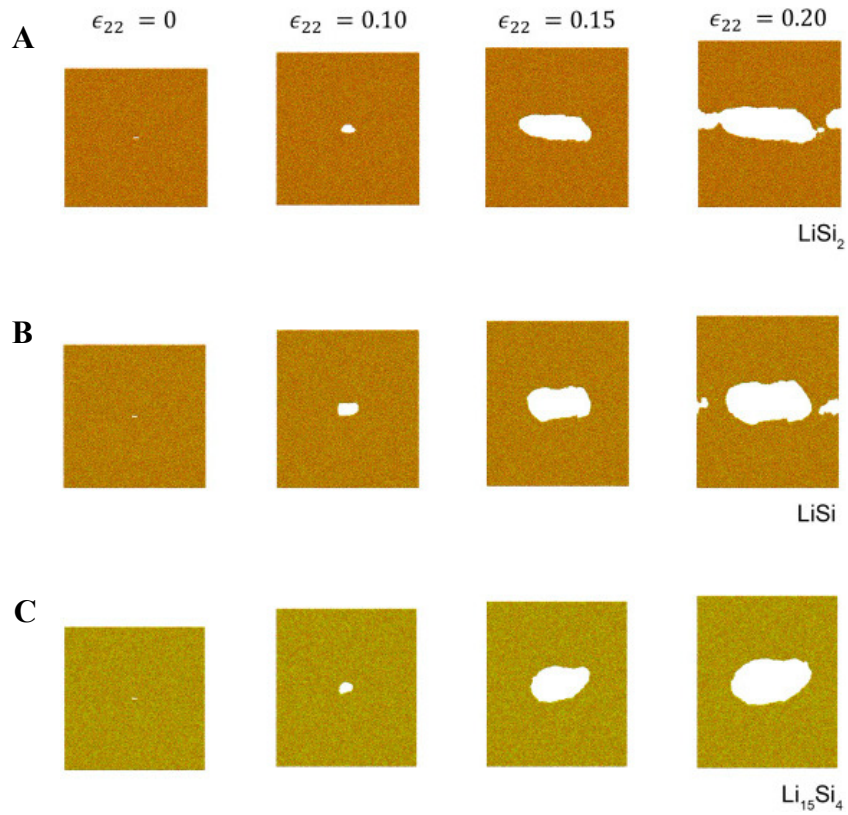
**Fig. 1: Sliding and delamination of  $\text{Li}_x\text{Si}$  thin film electrodes from the Cu current collector.** (A) Atomic structure of the interdiffused Li-Si-Cu interphase between a  $\text{Li}_x\text{Si}$  electrode and a Cu current collector. (B) Interface sliding facilitated by the formation of well-delineated and weakly bonded Si-Cu and Li-Cu crystalline atomic layers within this interphase structure. (C) Shear stress versus shear strain response demonstrating distinct regions of stress build-up and release leading to interface sliding, and stress accumulation leading to interface delamination.

## 2.2 Brittle-to-ductile transition of $\text{Li}_x\text{Si}$ electrodes

In contrast to pure silicon which is inherently brittle,  $\text{Li}_x\text{Si}$  alloys are able to undergo significant plastic deformation. Using first principle calculations, we show that  $\text{Li}_x\text{Si}$  electrodes exhibit a sharp transition from brittle to ductile behavior with increasing lithium content (**Fig. 2A**). The brittle behavior of pure Si and  $\text{LiSi}_2$  is associated with the interconnected network of strong Si-Si covalent bonds which have low bond stretchability of  $\sim 5\%$ ; breaking of these Si-Si bonds lead to sudden catastrophic failure (**Fig. 2B – top**). In contrast, the increased density of weaker Li-Li bonds which can be stretched to  $\sim 25\%$  in  $\text{LiSi}$  and  $\text{Li}_{15}\text{Si}_4$  causes the transition to ductile behavior (**Fig. 2B – bottom**).



**Fig. 2: Plasticity of  $\text{Li}_x\text{Si}$  electrodes.** (A) Stress-strain response of four  $\text{Li}_x\text{Si}$  alloys subjected to uniaxial straining. (B) Evolution of damage within  $\text{LiSi}_2$  (top) and  $\text{Li}_{15}\text{Si}_4$  (bottom) supercells with applied strain; brown lines represent Si–Si bonds, blue spheres represent the nanoporous regions.



**Fig. 3: Damage tolerance of  $\text{Li}_x\text{Si}$  electrodes.** Snapshots of the atomic configurations of (A)  $\text{LiSi}_2$ , (B)  $\text{LiSi}$ , and (C)  $\text{Li}_{15}\text{Si}_4$ , each with the same pre-existing flaw.

Our study demonstrates a sharp transition in the deformation behavior of  $\text{Li}_x\text{Si}$  from brittle to ductile as lithiation progresses. However, ductility and fracture toughness are two related, but different quantities,

since the latter refers to the alloy's flaw tolerance. Using molecular dynamics simulations, we introduce an initial flaw in the center of a periodic MD simulation box for  $\text{LiSi}_2$ ,  $\text{LiSi}$ , and  $\text{Li}_{15}\text{Si}_4$  model structures. We deform each  $\text{Li}_x\text{Si}$  structure, and show snapshots of the atomic configurations at various instants in **Fig. 3**. We show that crack propagates through and separates the entire  $\text{LiSi}_2$  structure (**Fig. 3A**), but only propagates partially through the  $\text{LiSi}$  structure (**Fig. 3B**). For the fully-lithiated  $\text{Li}_{15}\text{Si}_4$  structure, however, the flaw now becomes a cylindrical void and continues to grow with no signs of necking (**Fig. 3C**). We again attribute this high flaw tolerance of  $\text{Li}_{15}\text{Si}_4$  alloys to the large proportion of Li–Li bonds within the structure which can tolerate high stretches of  $\sim 22\%$  without breaking. Therefore, these MD simulations demonstrate that the flaw tolerance of  $\text{Li}_x\text{Si}$  alloys indeed increases with  $x$ , which is in agreement with our collaborative experiments.

### 3. List of Publications derived from BW Allocation

Wang, H., and Chew, H.B., Molecular dynamics simulations of plasticity and cracking in lithiated silicon electrodes. *Extreme Mechanics Letters*, (2016), in Press.

Harpale, A., Panesi, M., and Chew, H.B., Plasma-graphene interaction and its effects on nanoscale patterning. *Physical Review B*, 93 (2016), 035416.

Wang, H., Wang, X., Xia, S., and Chew, H.B., Brittle-to-ductile transition of lithiated silicon electrodes: Crazing to stable nanopore growth. *The Journal of Chemical Physics*, 143 (2015), 104703.

Li, R., and Chew, H.B., 'Closed and Open-Ended Stacking Fault Tetrahedra Formation along the Interfaces of Cu-Al Nanolayered Metals. *Philosophical Magazine*, 95 (2015), 2747-2763.

Wang, H., Hou, B., Wang, X., Xia, S., and Chew, H.B., Atomic-scale mechanisms of sliding along an interdiffused Li-Si-Cu interface. *Nano Letters*, 15 (2015), 1716-1721.

Harpale, A., Panesi, M., and Chew, H.B., Communication: Surface-to-bulk diffusion of isolated versus interacting C atoms in  $\text{Ni}(111)$  and  $\text{Cu}(111)$  substrates: A first principle investigation. *The Journal of Chemical Physics*, 142 (2015), 061101.

Li, R., and Chew, H.B., Planar-to-wavy transition of Cu/Ag nanolayered metals: A precursor mechanism to twinning. *Philosophical Magazine*, 95 (2015), 1029-1048.