Molecular Dynamics Simulations of Plasticity and Cracking in Lithiated Silicon Electrodes

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Abstract

First-principle calculations have provided critical insights into the deformation behavior of lithiated silicon electrodes in high-capacity lithium ion batteries, but quantitative interpretations have been limited by the size scales of these calculations. Here, we show that large-scale molecular dynamics (MD) simulations, based on the modified embedded atom method (MEAM) potential, are capable of describing the elastic softening and plastic behavior of Li_xSi alloys. In particular, our MD simulations at 0 K correctly reproduce the stress-strain response of Li_xSi alloys from Density Functional Theory (DFT) calculations across all Li concentrations, while matching the corresponding yield strength data from existing experiments at 300 K. Results from these MD simulations reveal a sharp transition in the atomic-scale plasticity mechanisms for Li_xSi with increasing Li content: from the breaking of Li-Si bonds at $x < 1$, to the breaking of Li-Li bonds at $x > 1$. The associated transition in the fracture behavior from brittle to ductile is due to the high stretchability of Li-Li bonds compared to Li-Si and Si-Si bonds.

Keywords: silicon electrode; plasticity; failure; molecular dynamics; interatomic potential

1. Introduction

Lithium ion batteries store energy by inserting lithium ions into solid electrodes. Conventional lithium ion batteries use graphite electrodes, which store a single Li atom per 6 C atoms. In comparison, Si electrodes have order-of-magnitude higher specific capacities, since each Si atom can theoretically bond with ~ 3.75 Li atoms [1]. However, this enormous storage of Li atoms in the Si electrode leads to unprecedented volume expansion of $\sim 300\%$ when the

electrode is fully-lithiated[2]. The huge inhomogeneous volume changes during cycles of lithiation and delithiation cause massive cracking of the Si electrode, eventually resulting in the loss of electrical contact and consequent capacity fade[3-5]. There is now increasing evidence that the mechanical degradation of Si electrodes under electrochemical cycling can be mitigated through the use of electrodes of small feature sizes, such as nanowires, nanoparticles, porous configurations, thin films, and core-shell structures[6-11]. Such nanostructured Si electrodes display significantly higher reversible charge capacity and longer cycle life, because the small characteristic dimensions of these electrodes lead to reduced energy release rate which is insufficient to drive crack propagation. More intriguingly, it is observed that these lithiated Si electrodes also undergo plastic deformation[12-15], which is in contrast to the brittle nature of unlithiated Si; how this plasticity behavior of Li_xSi influences the fracture properties is also contradictory. Early experiments have reported that both unlithiated and lithiated Si electrodes share similar fracture toughness values[16]. More recent experiments and computations concluded that the lithiation-induced plasticity of Li_xSi alloys results in ultra-high flaw tolerance[17,18].

A variety of continuum theories have been introduced to describe the coupled Li diffusion and elasto-plasticity behavior of Li_xSi alloys[19,20]. These models commonly account for finite deformation, as well as stress-gradient effects on Li diffusion. More recent models incorporate the contributions from lithiation kinetics and anisotropic motion of phase boundaries to better describe the lithiation of crystalline Si[21]. However, the physical properties used in these continuum models, including the elastic modulus and plastic yield strength of Li_xSi as a function of lithium content x , have to be calibrated from non-trivial experimental measurements or first-principle calculations[18,22-24]. More importantly, the underlying mechanisms of lithiation-induced deformation are inherently atomistic in nature. For example, the insertion of Li atoms into Si results in the breaking of covalent Si-Si bonds and the forming of ionic Si-Li bonds; such significant changes to the chemical bonding cannot be described by continuum models.

Density functional theory (DFT) calculations have been used to characterize the elasto-plastic behavior of amorphous Li_xSi alloys. Shenoy *et al.* demonstrated the elastic softening of Li_xSi alloys with increasing Li concentration[23]. Wang *et al.* showed the decreasing yield strength of Li_xSi with increasing Li content, and reported a sharp transition in the failure

response – from brittle to ductile – at intermediate Li concentrations[18]. These first-principle studies fully account for the bonding nature of Li_xSi under deformation. However, interpretations of the plasticity and fracture processes have been limited by the simulation domain sizes of ~ 150 atoms. In addition, temperature effects are not considered in these quantum-mechanical calculations. Accordingly, the DFT calculations are reported to over predict the yield strengths of Li_xSi compared to experimental measurements[22,25].

Molecular dynamics (MD) simulations offer an intermediate approach to link the DFT calculations to experiments. Two classes of interatomic potentials have so far been developed to describe the deformation behavior of Li_xSi alloys: the reactive-force-field (ReaxFF) potential by Ostadhosseinet *al.*[26] and the modified embedded atomic method (MEAM) by Cui *et al.*[27] In this paper, we compare the MD stress-strain predictions of Li_xSi alloys using both the ReaxFF and MEAM potentials. Results from the latter at 0 K are found to reproduce the elastic modulus and yield strength data of Li_xSi across all x from DFT calculations, while correctly matching the experimental measurements at 300 K. Our MEAM-based MD simulations further demonstrate that a critical simulation domain size of ~ 15 nm is necessary to capture the micromechanics of cleavage fracture at lower Li concentrations ($x < 1$) and the delocalized failure response at higher Li concentrations ($x \geq 1$). This transition in the fracture behavior from brittle to ductile corresponds with a transition in the atomic-scale plasticity mechanism, from the breaking of stiffer Li-Si bonds at low Li concentrations, to the breaking of highly stretchable Li-Li bonds at high Li concentrations.

2. Molecular Dynamics Modeling

Our MD simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[28]. The interatomic interactions are governed by MEAM and ReaxFF interatomic potentials specifically developed to describe the deformation behavior of pure Si and/or Li_xSi alloys[26,27,29]. We create amorphous Si, LiSi_2 , LiSi , $\text{Li}_{12}\text{Si}_7$ and $\text{Li}_{15}\text{Si}_4$ model structures via a rapid heating and quenching method first introduced in our previous DFT studies[18]. We start with realistic initial model structures, obtained by replicating and truncating the final periodic atomic Li_xSi configurations obtained from DFT[18], to achieve six fully-periodic cubic simulation boxes with initial edge dimensions of $d = 2.5, 4, 7, 10, 12$, and 15 nm for each

Li_xSi alloy. We perform an NVT calculation by subjecting each model structure to a temperature of 3000 K while keeping the box dimensions fixed; the temperature is maintained by a Berendsen thermostat for 10,000 MD steps. This temperature is higher than the melting point of Li, Si, and their compounds, and allows for sufficient intermixing between the Li and Si atoms. Each amorphous model structure is then quenched to the target temperature of 300 K (or 0 K) within 20,000 MD steps. We then perform an NPT calculation by equilibrating the structure at 300 K (or 0 K) for a further 30,000 MD steps while allowing the simulation box to relax with a Berendsen barostat to achieve a stress-free configuration. The final relaxed atomic configurations for a $\sim 4 \times 4 \times 4 \text{ nm}^3$ MD simulation box, based on the MEAM and ReaxFF interatomic potentials, are shown in Fig. 1. In all our simulations, we use a fixed time step of 1 fs.

We perform a pair correlation analysis to quantify the bonding characteristics for the Si-Si, Li-Si and Li-Li bonds within each Li_xSi model structure in Fig. 1. We show in Fig. 2 the radial distribution function (RDF) for each bond type. In general, the location of the RDF peaks for all three bond types corresponds to the equilibrium Si-Si, Li-Si and Li-Li bond distances of 0.245, 0.265, and 0.270 nm, respectively, as shown by dashed lines. Interestingly, both the MD model structures created using the MEAM and ReaxFF potentials have quantitatively very similar RDF distributions, even though both these potentials were formulated on very different theoretical foundations. The spread of the RDF for Si-Si bonds is consistently very narrow ($\pm 0.02 \text{ nm}$), indicating that Si-Si bonds are inherently stiff and have low stretchability of $\sim 8\%$. The spread of the RDF for Li-Si bonds is much larger ($\pm 0.04 \text{ nm}$), with bond stretchability of $\sim 15\%$. The spread of the RDF for Li-Li bonds is the largest ($\pm 0.06 \text{ nm}$), and is again consistent across all three Li_xSi structures. This implies that Li-Li bonds have the highest bond stretchability of $\sim 22\%$. The location of the RDF peaks and distribution of the RDFs are both in close agreement with model structures created by our prior DFT study[18], with exceptions of the DFT-calculated RDFs for Li-Li bonds of LiSi_2 and Si-Si bonds of $\text{Li}_{15}\text{Si}_4$ due to the limited number of Li and Si atoms in the respective DFT supercells.

We deform each of the above amorphous Li_xSi model structures by stretching the simulation box in the out-of-plane (x_2) direction, while rigidly constraining the in-plane dimensions of the box. MD simulations reveal that the deformation of Li_xSi can be driven by a competition between cavitation induced by hydrostatic stress and shear yielding induced by deviatoric

stress[30]. Here, our imposed uniaxial strain state subjects each Li_xSi structure to combined hydrostatic and deviatoric stresses. This strain-controlled loading state was previously used in our prior DFT calculations[18], in favor of conventional (uniaxial) stress-controlled loading, to achieve more stable and complete stress-strain curves. This is especially important for Li_xSi alloys with high Li content which undergo significant post-peak softening due to the nucleation and growth of nanopores. The use of the same loading state here facilitates direct comparison between our MD and DFT results. In our DFT calculations, uniaxial straining was imposed quasi-statically by subjecting the supercell to incremental 2% stretching in the out-of-plane direction, and allowing the atoms to relax to their equilibrium position quantum-mechanically after each increment. These calculations therefore resemble those from molecular statics at 0 K. Similarly, we incrementally deform our MD simulation box with 0.1% strain, by remapping all the atoms proportionally in the out-of-plane direction and allowing the atoms to relax to their local minimum energy configuration at 0 K before the next increment. This quasi-static loading eliminates the effect of strain rate on the deformation response. We obtain the “macroscopic” stress-strain curve by averaging the atomic virial stresses of the Li and Si atoms over the entire deformed box volume. We also obtain the deformation response of the Li_xSi alloys at 300 K by incrementally deforming the structure with 0.1% strain, but equilibrating the structure at a target temperature of 300 K which is maintained by a Berendsen thermostat for 0.5 ps after each increment.

3. Results

To ascertain the accuracy of the MEAM and ReaxFF interatomic potentials in describing the deformation response of Li_xSi alloys, we compare the stress-strain curves obtained from MD simulations using these potentials against those from prior DFT calculations[18]. Fig. 3 shows the von Mises stress-strain relationship for LiSi_2 , LiSi , and $\text{Li}_{15}\text{Si}_4$ alloys obtained from MD simulations based on the MEAM potential. These stress-strain curves are computed from MD model structures with edge dimensions of $d = 4$ nm at 0 K, as well as $d = 4, 7$, and 15 nm at 300 K. The corresponding stress-strain results from DFT calculations are denoted by open symbols interconnected by dashed lines. The stress-strain curves from DFT display an initial linear elastic response followed by plastic yielding to reach peak stresses of 3, 2.5, and 1.5 GPa for LiSi_2 , LiSi , and $\text{Li}_{15}\text{Si}_4$, respectively. Beyond this point, the LiSi_2 alloy undergoes sudden loss of stress-

carrying capacity which suggests catastrophic failure, while the LiSi and $\text{Li}_{15}\text{Si}_4$ alloys exhibit more gradual softening due to the cavitation and growth of nanopores. The stress-strain curves obtained from our MD simulations at 0 K for all three Li_xSi alloys are remarkably in good agreement with DFT calculations. This suggests that the MEAM potential well captures the theoretical elasto-plastic behavior of Li_xSi alloys, although the MD simulations at 0 K are unable to capture the failure/softening response exhibited by DFT. At temperatures of 300 K, the tensile yield stresses for all three Li_xSi alloys are reduced by several-folds, and now exhibit a distinct loss of stress-carrying capacity beyond a critical strain. Because of the statistical nature of the associated failure/cavitation process, this critical strain decreases with increasing model sized, at least up to a certain point, although d has no visible influence on the elasto-plastic properties. Therefore, a sufficiently large MD simulation box is needed to simulate the failure of Li_xSi alloys. We further note that the critical strains for $d = 15$ nm at 300 K are very close to those predicted by DFT calculations at 0 K. Fig. 4 compares the von Mises stress-strain relationship from MD simulations based on the ReaxFF potential versus DFT calculations for LiSi_2 , LiSi, and $\text{Li}_{15}\text{Si}_4$ alloys. The ReaxFF-based MD simulations correctly predict the elastic softening and decreasing yield strength of Li_xSi with increasing Li content. Unlike the MEAM-based MD results, however, the peak tensile stress values at 0 K obtained with ReaxFF are quantitatively different from those from DFT calculations. Specifically, the ReaxFF-based MD simulations at 0 K over-predict the peak yield stress values for LiSi_2 and LiSi by 44% and 36%, respectively, but accurately predict the yield stress value of ~ 1.2 GPa for $\text{Li}_{15}\text{Si}_4$.

We summarize in Fig. 5 the elastic modulus and peak tensile yield stress values versus the lithium fraction (defined as the ratio of Li atoms to the total number of atoms) of five Li_xSi model structures obtained from our MEAM- and ReaxFF-based MD simulations conducted at 0 K and 300 K. These results are based on our $d = 4$ nm MD simulation box, though we note that both the elastic modulus and yield stress are independent of d . To account for statistical variations, we conducted MD simulations to obtain the stress-strain response of 5 different amorphous Li_xSi configurations. We find the error bars for both the elastic modulus and yield strength to be negligible for our $d = 4$ nm model structure. We also include the results of DFT calculations [18], as well as those from experimental measurements [13,22,24,31], for comparisons with our 0 K and 300 K MD results respectively. Results from our ReaxFF- and MEAM-based MD simulations show that the elastic modulus and yield strength of Li_xSi both decrease linearly with

Li content and closely follow the rule-of-mixtures. In fact, the elastic modulus predictions from both potentials are very similar and are generally in good agreement with DFT calculations at 0 K, but slightly under-predict the experimental values at 300 K. The ReaxFF-based prediction of the tensile strength of pure Si at 0 K is in very good agreement with DFT calculations. We remark that pure amorphous Si does not actually undergo yielding but fails in a brittle manner without plastic deformation, and σ_y here for pure Si represents the tensile strength. With this exception, the MEAM-based MD simulations are found to more accurately match the DFT results for lithiated Si at 0 K. More importantly, the tensile yieldstrength predictions from these MEAM-based MD simulations at 300 K are also in perfect agreement with experimental yield strength measurements. In addition to the high accuracy of the MEAM potential, we find the computations based on this potential to be ~ 40 times faster than those based on ReaxFF potential. Our MD simulations in the following will be based on the MEAM potential.

In previous DFT calculations, it was concluded that the surprising plasticity behavior of Li_xSi , in contrast to the brittle behavior of pure Si, is due to the nucleation and growth of nanopores[18]. Because of the limited sizescale of the supercells in DFT, however, the observed porosity is in fact angstrom-sized voids caused by localized bond breaking. Using MD simulations, we seek to understand how these angstrom-scale voids develop into actual nanometer-scale voids, and how these nanopores in turn grow and coalesce. Fig. 6 shows the evolution of porosity f versus the applied strain ϵ_{22} for different MD model sizes of $d = 2.5, 7, 10, 12$, and 15 nm. We again focus on LiSi_2 , LiSi , and $\text{Li}_{15}\text{Si}_4$ alloys, which cover the spectrum of model structures with low, intermediate, and high Li content. For each alloy, we divide the deformed MD simulation box into regular grids, each of $(0.15)^3 \text{ nm}^3$. We consider each grid as a void if there are no atoms within a 0.3 nm radius, which is slightly larger than the equilibrium Li-Li, Li-Si and Si-Si bond distances. We then sum up the total void volume in the box, and divide this by the current deformed box volume to get f . For all three Li_xSi alloys, the porosity versus strain curves become model-size-independent only with $d = 12 \text{ nm}$ and larger. For the LiSi_2 alloy, the porosity remains negligible up to a critical strain of $\epsilon_{22} = 0.2$, as seen for $d = 12$ or 15 nm , upon which f dramatically increases indicating catastrophic brittle-like fracture; we remark that the use of smaller model sizes of $d = 2.5 \text{ nm}$ may lead to the incorrect interpretation of a more gradual failure response. For the LiSi alloy, the critical strain for the onset of pore growth

occurs much earlier at $\epsilon_{22} = 0.08$; the pore growth rate is also more gradual, suggesting a stable ductile failure response. For the fully-lithiated $\text{Li}_{15}\text{Si}_4$ alloy, nucleation of nanopores is delayed and initiates only at $\epsilon_{22} = 0.12$. At this critical strain, the initial void growth rate is fairly rapid, though not catastrophic as in LiSi_2 ; further loading slows down the pore growth rate to reach a steadystate similar to LiSi .

Next, we examine the nanopore nucleation, growth and coalescence process for LiSi_2 , LiSi and $\text{Li}_{15}\text{Si}_4$ alloys. We adopt relatively large $d = 15$ nm MD model structures where the porosity evolution across all three alloys becomes model-size independent (Fig. 6). For each of these model structures, we filter the deformed MD box to display only the voids within the structure, which are shaded grey in Figs. 7a-9a, a cross-sectional cut (dashed lines) of the corresponding atomic configurations and bonding structures in Figs. 7b-9b. For the LiSi_2 alloy in Fig. 7, damage initiates at $\epsilon_{22} = 0.195$. Within 1.5% strain increment, this damage spreads across the entire cross-section of the simulation box to cause cleavage fracture. The deformed atomic configurations at $\epsilon_{22} = 0.195$ show the presence of incipient nanopores (angstrom-sized voids), which become more well-defined at $\epsilon_{22} = 0.20$. Close-up view shows that these incipient nanopores originate from the breaking of Si-Li bonds, which result in the plasticity behavior of LiSi_2 (Fig. 3a). Observe that these incipient nanopores are well-separated by interconnected chains of Si-Si bonds, which prevent them from developing into true nanometer-sized pores. The Si-Si chains separating the incipient nanopores eventually break at $\epsilon_{22} = 0.2$. Cracks subsequently form and propagate along the path which locally has the highest density of weaker Li-Si bonds, as evidenced by the broken Li and Si bonds along the sharp fracture surface.

For the LiSi alloy in Fig. 8, significant void growth already occurs at $\epsilon_{22} = 0.12$, as shown by the presence of two adjacent ~ 2 and ~ 4 nm diameter nanopores within the structure. These nanopores stably grow, and coalesce at $\epsilon_{22} = 0.14$. The eventual formation of a void sheet at $\epsilon_{22} = 0.16$ results in the softening stress-strain response (Fig. 3b). This ductile fracture process results in a much rougher fracture surface, as compared to the brittle failure response of LiSi_2 . The corresponding cross-sectional views of the deformed atomic configurations (Fig. 8b), and the associated close-up views of the bonding configurations (Fig. 8c), show that the nanopores primarily grow and coalesce by the breaking of Li-Li and Li-Si bonds, while the few Si-Si bonds in the LiSi structure remain mostly intact.

For the fully-lithiated $\text{Li}_{15}\text{Si}_4$ alloy in Fig. 9, a distinct $\sim 1\text{nm}$ diameter nanopore first nucleates at $\epsilon_{22} = 0.12$. Three additional nanopores of diameters $\sim 1\text{-}2\text{nm}$ subsequently nucleate at $\epsilon_{22} = 0.13$, each growing independently of one another. This delocalized growth of nanopores explains why the porosity evolution curves for $\text{Li}_{15}\text{Si}_4$ in Fig. 6c are not as strongly dependent on the model size d as compared to LiSi or LiSi_2 . The nanopores eventually coalesce at $\epsilon_{22} = 0.14$, causing the loss of stress-carrying capacity for $\text{Li}_{15}\text{Si}_4$ (Fig. 3c). The cross-sectional view of the deformed atomic configuration at $\epsilon_{22} = 0.12$ shows distinct clusters of Li rich regions encapsulated by networks of Si-Si and Si-Li chains. This clustering of Li atoms is unlike our prior $\text{Li}_{15}\text{Si}_4$ structures obtained from DFT, where the 32 Si atoms are relatively evenly-dispersed among the 120 Li atoms due to the limited supercell size, as shown by the RDF peaks in Fig. 2. Close-up view shows that strain is localized within these Li-rich clusters, which are potential sites for nucleation of nanopores. Since these Li-rich clusters are evenly distributed throughout the entire MD simulation box, the damage process is more delocalized. At $\epsilon_{22} = 0.13$, the breaking of Li-Li bonds within the Li-rich clusters results in the sudden formation of multiple discrete nanopores within the structure. While this causes a sudden spike in the porosity in Fig. 6c, the nanopores do not immediately coalesce because they are encapsulated by strong Si-Si and Si-Li bond networks. Instead, coalescence occurs gradually in a controlled fashion by the breaking of Li-Si bonds, as shown at $\epsilon_{22} = 0.14$.

4. Discussions

Our above results demonstrate that the plasticity and cracking of Li_xSi alloys are closely-related to the fraction of Si-Si, Si-Li, and Li-Li bonds within the structure. At low Li concentrations, the peak tensile yield strength of the Li_xSi alloy is at its highest, since the structure primarily comprises of covalent Si-Si bonds. The breaking of weaker ionic Li-Si bonds allows the alloy to undergo plasticity, but these broken Li-Si bonds are unable to fully-develop into nanopores because of the interconnected chains of Si-Si bonds within the structure. The eventual scission of Si-Si bonds results in brittle fracture and the fracture surface remains very sharp due to the absence of significant void growth during plasticity. At intermediate Li concentrations, plasticity of the Li_xSi alloy occurs by the breaking of Li-Si bonds or/and the breaking of even weaker metallic Li-Li bonds. Since the fraction of Si-Si bonds is now smaller, the broken Li-Si or Li-Li bonds readily develop into nanopores, which explains the early onset of

void growth in Fig. 6b. These nanopores in turn grow and coalesce to form a void sheet. This juncture at $x \sim 1$ marks the transition in the fracture behavior of Li_xSi from brittle to ductile. At high Li concentrations, the Li_xSi alloy is now able to undergo extreme deformations due to the high proportion of Li-Li bonds, which have bond stretchability of $\sim 22\%$ compared to $\sim 15\%$ and $\sim 8\%$ for Si-Li and Si-Si bonds (Fig. 2). This high bond stretchability delays the development of nanopores (compare Fig. 6c with Fig. 6b). Once these nanopores form resulting in the observed initial jump in porosity, subsequent void growth occurs more gradually (Fig. 6c). Each nanopore now grows independently of the surrounding nanopores, again because of the high Li-Li bond stretchability, which delays void coalescence and failure. Hence, the fully-lithiated $\text{Li}_{15}\text{Si}_4$ alloy will be considerably more ductile compared to LiSi . Much of the strength of this alloy now comes from the fewer Li-Si bonds within the structure, giving rise to the low tensile yield strength.

Our study demonstrates a sharp transition in the deformation behavior of Li_xSi 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. Are Li_xSi alloys with high Li content truly more flaw-tolerant than those with low Li content? Our recent nanoindentation experiments appear to support this notion [17], though earlier experiments have alluded that the fracture toughness of Li_xSi alloys is independent of x [16]. Here, we introduce an initial flaw in the form of a 1.5 nm by 0.5 nm through-crack located in the center of the periodic MD simulation box of $d = 15 \text{ nm}$, for the LiSi_2 , LiSi , and $\text{Li}_{15}\text{Si}_4$ model structures. To prevent the flaw from closing, we impose an initial uniaxial strain of 5% by proportionally displacing the atoms in the simulation box and allowing the system to relax at the temperature of 300 K . Thereafter, we continue deforming each Li_xSi structure, and show snapshots of the atomic configurations at various instants in Fig. 10. At $\epsilon_{22} = 0.1$, the initial sharp flaw becomes oblate for LiSi_2 , but is distinctly more circular for $\text{Li}_{15}\text{Si}_4$. At $\epsilon_{22} = 0.2$, crack propagates through and separates the entire LiSi_2 structure, but only propagates partially through the LiSi structure. 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. We 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 Li_xSi alloys indeed increases with x , which is in agreement with our recent experimental results [17].

We remark that the MD simulations conducted here have provided mechanistic insights into the plasticity and cracking behavior of Li_xSi alloys at scales not within the capabilities of DFT. This opens up unique possibilities for future simulation-based nanostructured electrode design. The accuracy of these MD simulations hinges on the interatomic potentials. The bulk of our current MD studies was carried out using the MEAM potential by Cui *et al.*[27]. This MEAM potential was found to be highly accurate in replicating the elasto-plastic responses from DFT calculations at 0 K and experimental measurements at 300 K (Fig. 5). More impressively, the associated bond-breaking mechanisms from these MD simulations were found to be in very good agreement with our prior DFT studies[18]. In comparison, the MD simulations based on the ReaxFF potential by Ostadhossein *et al.*[26] tend to over-predict the yield strengths of Li_xSi alloys (Fig. 5b). Nevertheless, the ReaxFF potential is specifically designed to account for chemical bond breaking and bond formation processes, and we find the underlying plasticity and cracking mechanisms associated with the ReaxFF potential to be largely similar to those from our MEAM-based MD simulations.

5. Conclusion

In summary, MD simulations have provided quantitative insights into the deformation behavior of Li_xSi alloys. The MEAM-based MD simulations at 0 K correctly reproduce the stress-strain response of Li_xSi alloys from DFT calculations, while matching the yield strength data from experiments at 300 K. These MD simulations demonstrate the brittle-to-ductile transition of Li_xSi alloys, as well as the increasing flaw tolerance, with increasing Li content. This transition is largely associated with increasing proportion of highly-stretchable Li-Li bonds at the expense of stiffer Si-Si bonds. In addition, these simulations have identified the breaking of Li-Li and/or Li-Si bonds as the precursor for nanopore nucleation and growth. These atomistic mechanisms fully explain the macroscopic plasticity and fracture behavior of Li_xSi alloys.

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Figure Captions

FIG. 1. Final relaxed atomic configurations of amorphous Si, LiSi₂, LiSi, Li₁₂Si₇ and Li₁₅Si₄ after rapid heating and quenching in MD. The simulations are conducted using $\sim 4 \times 4 \times 4$ nm³ MD simulation boxes, and are based on the (a) MEAM and (b) ReaxFF interatomic potentials. The Si and Li atoms are colored in orange and yellow, respectively.

FIG. 2. Comparison of the RDF distributions for Si-Si, Li-Si, and Li-Li bonds within LiSi₂, LiSi, and Li₁₅Si₄ alloys, created by MD simulations based on the ReaxFF (red) and MEAM potentials (blue), as well as prior DFT calculations (black). Dashed vertical lines denote the equilibrium bond distance for the corresponding bond type.

FIG. 3. Comparison of the vonMises effective stress-strain response for (a) LiSi₂, (b) LiSi, and (c) Li₁₅Si₄ from MD simulations based on the MEAM potential versus DFT calculations.

FIG. 4. Comparison of the vonMises effective stress-strain response for (a) LiSi₂, (b) LiSi, and (c) Li₁₅Si₄ from MD simulations based on the ReaxFF potential versus DFT calculations.

FIG. 5. Summary of elastic modulus and tensile yield strength of Li_xSi alloys at different lithium fractions from MEAM- and ReaxFF-based MD simulations, DFT calculations, and experiments.

FIG. 6. Simulation box size effects on the porosity evolution versus applied strain for (a) LiSi₂, (b) LiSi, and (c) Li₁₅Si₄ alloys.

FIG. 7. Cleavage fracture process for LiSi₂. (a) Porosity evolution within the model structure at three instances. (b) Cross-sectional views of the atomic configurations taken along the dashed lines in (a). The Si and Li atoms are colored in orange and yellow, respectively.

FIG. 8. Ductile fracture process for LiSi. (a) Porosity evolution within the model structure at three instances. (b) Cross-sectional views of the atomic configurations taken along the dashed lines in (a). (c) Close-up view of the Li-Li and Li-Si bond breaking process. The Si and Li atoms are colored in orange and yellow, respectively.

FIG. 9. Ductile fracture process for $\text{Li}_{15}\text{Si}_4$. (a) Porosity evolution within the model structure at three instances. (b) Cross-sectional views of the atomic configurations taken along the dashed lines in (a). The Si and Li atoms are colored in orange and yellow, respectively.

FIG. 10. Snapshots of the atomic configurations for (a) LiSi_2 , (b) LiSi , and (c) $\text{Li}_{15}\text{Si}_4$, each with the same pre-existing flaw within the model structure, demonstrating increasing flaw tolerance with Li content. The Si and Li atoms are colored in orange and yellow, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10