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Elastic softening of amorphous and crystalline Li–Si Phases with increasing Li concentration: A first-principles study

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ABSTRACT

Knowledge of the elastic properties of Li–Si alloys as a function of Li concentration is crucial in the development of reliable deformation and fracture mechanics models for Si anodes in Li-ion batteries. Here, we have studied these properties using first-principles calculations for both amorphous and crystalline phases observed during lithiation of Si anodes. In the case of crystalline alloys, we present the anisotropic elastic tensors as well as the homogenized Young's, shear, and bulk moduli and the Poisson's ratios. We find that while these moduli decrease in an approximately linear manner with increasing Li concentration leading to significant elastic softening (by about one order of magnitude) in both crystalline and amorphous systems, the Poisson's ratios remain in the range of 0.05–0.20 and 0.20–0.30 in the case of crystalline and amorphous systems, respectively. Further, for a given Li concentration, we find that the amorphous structures are elastically somewhat softer than their crystalline counterparts, the difference being more significant (about 30–40%) in Li-poor phases. Our results underscore the importance of including the concentration dependence of elastic constants in the analysis of stress and deformation fields during lithiation and de-lithiation of Si anodes.

1. Introduction

Advanced energy storage technologies for transportation industries require further improvement of the power, energy density, and durability of Li-ion batteries for use in hybrid electric vehicles (HEV), plug-in HEV (PHEV), and all-electric vehicles (EV). Currently, the negative electrode material used in most Li-ion batteries is graphite, which forms lithium–graphite intercalation compounds (Li-GIC) [1,2]. Compared to graphite, Si can store ~10 times more Li, as the gravimetric energy densities are 3572 mAh g^{-1} for Si, and 372 mAh g^{-1} for graphite. However, this extremely high capacity of Si is associated with massive structural changes and volume expansion on the order of 300% [3–5], resulting in electrode particle fracture, disconnection between the particles, capacity loss, and thus very limited cycle life.

Wolfenstine [6] demonstrated that using the Young's modulus, the fracture toughness, and the volume change, a critical particle size for low capacity fade could be estimated with analytical modeling. Mathematical models of deformation and corresponding stress fields during lithiation and de-lithiation of idealized electrodes have been recently developed [7–14]. In all of these continuum-level models, the intrinsic mechanical properties of electrodes, such as Young's modulus and Poisson's ratio are assumed to be constants, independent of Li concentration. This is not surprising, given the lack of experimental data as well as theoretical calculations. Recently, Qi et al. used density functional theory (DFT) to demonstrate that the polycrystalline Young's modulus (E) of graphite increases linearly with Li concentration, and triples when graphite is fully lithiated to LiC_6 [15]. The lithiation process of Si is different from the interaction process of Li in graphite, where Li ions are intercalated between the graphite sheets during the charging cycle and removed during discharge with minimal structural change and a 10% variation in volume. Si experiences large structural changes upon lithiation and de-lithiation. If Si is lithiated at high temperature (415 °C) in a LiCl–KCl melt, crystalline structures of Li_7Si_3, $Li_{12}Si_7$, $Li_{13}Si_4$, and $Li_{22}Si_5$ phases will form; these structures can also be found in the equilibrium phase diagram prepared metallurgically [16]. At room temperature, in a Li-ion battery cell, when Li–Si is electrochemically cycled, crystalline Si becomes amorphous Li_xSi as it is lithiated [17]. If Si is lithiated completely, the crystalline $Li_{15}Si_4$ phase is obtained [18–19]. Using an in situ stress measurement technique, rapid rise in compressive stress has very recently been observed during lithiation of Si anodes ultimately leading to plastic flow [20]. However, data on the elastic properties and failure of Li–Si alloys is currently not available to quantitatively model these measurements.

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Table 1
Equilibrium structural parameters for Li, Si, and Li_xSi alloys obtained from PAW-GGA calculations. The number of irreducible *k* points used in the DFT calculations in each case is also given in the table.

Phase	*x*	Space group	*a* (Å)	*b* (Å)	*c* (Å)	Volume (Å^3)	*k*-points
Si	0.000	$Fd\bar{3}m$	5.472	5.472	5.472	163.814	20
LiSi	0.500	*I41/a*	9.357	9.357	5.746	503.071	144
$Li_{12}Si_7$	0.632	*Pnma*	8.532	19.612	14.302	2393.069	4
$Li_{13}Si_4$	0.765	*Pbam*	7.914	15.084	4.429	528.725	8
$Li_{15}Si_4$	0.789	$I\bar{4}3d$	10.595	10.595	10.595	1189.472	32
$Li_{22}Si_5$	0.815	*F23*	13.189	13.189	13.189	1622.280	88
Li	1.000	$Im\bar{3}_m$	3.442	3.442	3.442	40.796	20

Recently, the electronic structure, lattice vibrations, and the Birch-Murnaghan equation of state of crystalline phases was studied by Chevrier et al. using first-principles calculations [21,22]. However, the Young's and the shear moduli and the Poisson's ratio necessary for analyzing fracture and shear flow during lithiation were not considered in their study. Similarly, while the structures of amorphous phases have been considered, there is no information available on the elastic properties on amorphous alloys. In this article, we compute the complete elastic constants of Li–Si crystalline and amorphous phases, using first-principles calculations. Our goal is to derive a functional form of the relationship between the averaged elastic modulus and the Li concentration in the alloy, so that this information can be readily used in continuum-level models of deformation and failure. In the case of crystalline alloys, we present anisotropic elastic constant tensors as well as orientationally averaged Young's, shear, and bulk moduli and the Poisson ratios. In the case of amorphous alloys we directly compute these moduli using structures generated using ab initio molecular dynamics simulations. We find that the moduli of Li–Si alloys decrease almost linearly with Li concentration and it drops to about an order of magnitude of its original value of Si, when it is fully lithiated (in the $Li_{15}Si_4$ and $Li_{22}Si_4$ phases). The observed elastic softening is explained by considering the charge–density and atomic bonding in lithiated alloys. Our calculations also show why the amorphous alloys are generally softer than their crystalline counterparts. These results suggest that mechanical modeling of Si anode deformation and fracture needs to account for varying material and elastic properties with Li concentration.

2. Methods

DFT calculations were performed using the Vienna Ab Initio Simulation (VASP) Package [23,24] with the Projector Augmented Wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation for exchange and correlation. For crystalline phases, the structures of the alloys were obtained from crystal structure database and from experimental work [25–30]. From convergence studies, we determined the kinetic energy cutoff in the plane wave expansion to be 300 eV. The optimized lattice parameters of the crystalline Li–Si phases obtained from our calculations are summarized in Table 1. The number of irreducible *k* points used for each of the Li–Si alloy phases is also given in this table. The structural data in Table 1 agrees well with experimental studies and previous theoretical work [18,19,31–37].

Amorphous systems were created using ab initio molecular dynamics (MD) simulations using the VASP package. We started with a periodic super cell that consists of the alloy in its crystalline form (typically with 100–150 atoms). The cell was then heated to a temperature much larger than the melting temperature of the crystalline phase (3000–4000 K). The system was allowed to equilibrate at this temperature for 5000 MD time steps (each MD time step = 1 fs). To obtain the amorphous phase, we then cooled these structures to room temperature at the rapid rate of 200 K per 200 MD time steps, *i.e.*, we sequentially reduced the temperature by 200 K and let the system evolve for 200 MD steps. The geometries obtained at room temperature were then relaxed with an atomic force tolerance of 0.01 eV Å^{-1}. In our relaxation simulations, along with the atomic coordinates, we also allowed variations of the dimensions as well as the shape of the super cell. For a given Li composition up to five statistically independent realizations of the amorphous structures were created. We emphasize that our method for generating the amorphous structures is very different from the protocol employed in Ref. [38]. In particular, we do not rely on initial atomic configurations obtained from empirical potentials. Our method is based entirely on the DFT formalism and should therefore be more accurate. Furthermore, the method we have outlined is simple to implement as it employs well-established MD time-integration techniques. Nonetheless, we have found that our calculated formation energies for amorphous systems (*c.f.* Table 2) are in very good agreement with the results obtained by Chevrier et al. [38].

In case of crystalline systems, elastic constants were determined by computing the energies of deformed unit cells. For cubic type phases, Si, $Li_{15}Si_4$, and Li, distortions with tetragonal and orthorhombic shear, and isotropic distortion along the three lattice vectors were applied to obtain three independent elastic constants C_{11}, C_{12}, and C_{44} (all elastic constants are expressed using the Voigt notations [39]). For the tetragonal Li–Si phase, we applied six different deformation modes to compute C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66}. For $Li_{12}Si_7$ and $Li_{13}Si_4$, expansion along three high-symmetry directions, three monoclinic distortions, and three orthorhombic distortions were applied to obtain nine independent elastic constants. We allowed relaxation of the atomic positions in all the strained supercells.

Next, we discuss the methodology used to compute the elastic constants of amorphous alloys. Since amorphous phases are isotropic and are therefore characterized by two independent elastic constants, the bulk modulus B and the modulus C_{11}. We first computed B and C_{11} and once these quantities were known, we used the relations between different elastic constants [39] to deduce the Young's modulus, the shear modulus, and the Poisson's ratio. Note that the basis vectors of the optimized amorphous supercell obtained using our relaxation procedure need not in

Table 2
Comparison of the calculated formation energies with the work of Chevrier et al. [38] for amorphous Li–Si phases. The formation energy was calculated using expression: $E_f = E(Li_xSi) - [xE(Li) + E(Si)]$, where x is the number of Li atoms per Si atoms, $E(Li_xSi)$ is the total energy of the Li_xSi structure divided by the number of Si atoms used in the calculation, $E(Li)$ is the total energy of the single Li atom elemental BCC Li (−1.895 eV), and $E(Si)$ is the total energy of a single Si atom in elemental Si diamond lattice (−5.422 eV).

Phase (x in Li_xSi)	Formation energy E_f (eV)	
	Our results	Chevrier et al. [38]
a-LiSi ($x = 1$)	−0.20	−0.22
a-$Li_{12}Si_7$ ($x = 1.7$)	−0.40	−0.44
a-$Li_{15}Si_4$ ($x = 3.75$)	−0.88	−0.80