



A continuum model of deformation, transport and irreversible changes in atomic structure in amorphous lithium–silicon electrodes



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ABSTRACT

Recent experiments and atomic scale computations indicate that the standard continuum models of diffusion in stressed solids do not accurately describe transport, deformation and stress in Li–Si alloys. We suggest that this is because classical models do not account for the irreversible changes in atomic structure of Si that are known to occur during a charge–discharge cycle. A more general model of diffusion in an amorphous solid is described, which permits unoccupied Si lattice sites to be created or destroyed. This may occur as a thermally activated process; or as a result of irreversible plastic deformation under stress. The model predicts a range of phenomena observed in experiment that cannot be captured using classical models, including irreversible changes in volume resulting from a charge–discharge cycle, asymmetry between the tensile and compressive yield stress, and a slow evolution in mechanical and electrochemical response over many charge–discharge cycles.

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1. Introduction

There is great interest in using Si as a high-capacity anode in Li ion batteries [1]. Its widespread use has been limited by large capacity losses under cyclic charging. Mechanical degradation, driven by the large stresses induced by volume changes in lithiated Si, is believed to be the leading cause of this capacity loss. Managing these stresses through innovative electrode configurations or microstructures is a promising approach to making Si a practical electrode material [2–7]. This has motivated a large number of recent experimental, theoretical and computational studies of the electrochemical and mechanical response of Li–Si alloys [8].

In particular, recent in-situ observations of deformation in Si resulting from Li insertion, as well as controlled measurements of stresses generated in Si electrodes have revealed that: (i) Si increases its volume by roughly a factor of three when fully lithiated [9]; (ii) Crystalline silicon transforms to an amorphous structure during the first lithiation cycle, and thereafter remains amorphous [9,10]; (iii) A sharp phase boundary develops between crystalline and amorphous Si. The velocity of this phase boundary is a function of the electrode over-potential and is strongly dependent on the orientation of the phase boundary with respect to the underlying crystal [11,12]; (iv) The mechanical stress-vs-strain response of amorphous Li–Si is inelastic and irreversible. This was

first deduced from experimentally measured stress-vs-capacity curves for thin film electrodes, which show reversible linear elastic behavior at small stresses, and an approximately constant flow stress around 1 GPa [13]. The elastic modulus and flow stress are functions of composition and the rate of charging [14,15]. More recently, rate dependent plastic flow has also been observed directly by nanoindentation tests [16].

Guided by these experiments, a number of models of concurrent transport and deformation in Li–Si alloys have been developed. These have calculated the thermodynamic driving forces for diffusion of Li in Li–Si, taking into account plasticity and large changes in volume [17]; have determined the influence of stresses on electrochemical reactions [18]; have proposed stress–strain relations for lithiated Si; and have treated the phase transformation in lithiated silicon using both traditional Cahn–Hilliard type phase-field methods suitably extended to include plasticity [19], as well as using models in which the diffusion coefficient is concentration dependent [20]. Systematic comparisons between theory and experiment have been used to determine values for material properties of Li–Si in these models [14,15]. The material models have been used to calculate stress distributions in a number of representative electrode structures, including thin film electrodes [14]; patterned islands [4], and particles [21–23].

Despite these promising results, there are indications from both experiments and atomistic simulations that existing models of Li–Si are incomplete. For example, the low flow stress of Li–Si compared to amorphous Si is somewhat mysterious. Ab-initio

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atomistic simulations have suggested that the Li insertion process itself reduces the flow stress, since the flow stress of a volume element with a fixed Li concentration subjected to a mechanical strain exceeds the stresses that develop in a constrained volume element during the Li insertion process itself [24]. Reactive force-field molecular dynamics simulations [25] do not predict this difference between mechanical and insertion induced flow, but suggest that the tensile and compressive flow stresses of lithiated Si differ, which is not predicted by continuum models. In addition, while models are able to capture most qualitative features of experimentally measured stress-vs-capacity curves, there are features on the experimental data that are not consistent with models, particularly for the first lithiation cycle [14]. The discrepancies have been attributed to capacity loss to SEI formation, but it is possible that other processes play a role. Recent in-situ observations of deformation in amorphous thin film Si electrodes also revealed the formation of a propagating interface that resembles a phase boundary in these materials [26]. It is not clear what physical mechanism gives rise to this phenomenon, and it would not be predicted by the conventional models of diffusion in a random solid solution. Recent measurements of volume changes in Si electrodes during lithiation also suggest that the change in volume is irreversible [27]. Again, this is not consistent with classical models of transport in solids.

Motivated by these discrepancies, there have been several recent proposals to extend the conventional theory of diffusion in solids to include more complex physical processes that might accompany Li insertion into Si. Brassart and Suo have proposed a 'reactive flow' model for plasticity in amorphous Li-Si, in which the usual relationship between concentration and chemical potential is replaced by a rate dependent form, which characterizes a dissipative insertion reaction [28,29]. A thermodynamic consequence of this assumption is that the chemical potential must also influence the flow stress of the material, leading to a strong coupling between mechanical behavior and chemical reactions that is not present in the classical theory of diffusion in stressed solids. Zhang et al. [30] have developed a somewhat similar model, in which Li can exist at a point in the Si in two states; a 'reacted' state, and an 'unreacted' state; the transition from one state to the other is dissipative and changes the volume of the alloy. Another model has been further developed by Drozdov [31], who uses a more elaborate description of the solution thermodynamics, as well as strongly concentration dependent diffusion coefficients.

In this paper, we adopt a somewhat different viewpoint. Instead of generalizing the thermodynamics of the Li insertion process, we extend traditional descriptions of transport in solids to take into account the structural changes that occur as a result of Li insertion into Si. Recent models of Li-Si [14,15,17–19] are all based on extensions of the Larche–Cahn model of diffusion in solids [32–34], which assumes that transport takes place by discrete atomic hops on a fixed lattice. The original Larche–Cahn model was intended to model only elastic solids, in which the lattice can deform in response to stress, but this deformation is reversible. Larche and Cahn also stipulated that lattice sites can only be created and destroyed at lattice defects such as interfaces, dislocations, or grain boundaries [34]. If this model is applied to Li-Si, it implies that Li insertion into a stress free material element simply expands or shears the lattice, changing the distance between neighboring atoms and possibly bond angles, but without affecting the underlying lattice structure. The volume of a stress free solid is consequently a unique (but possibly nonlinear) function of the Li concentration. It is known that deformations resulting from Li insertion are not generally reversible, but extensions of the Larche–Cahn model to Li-Si [14,17–19] have simply added the possibility of irreversible plastic deformation of the underlying lattice to the original model. The assumption is that plasticity rearranges the underlying lattice but does not change the number of lattice

sites, their coordination, or the volume of the solid. In consequence, the volume expansion remains a reversible function of Li concentration. The recent extensions by Zhang et al. [30] and Drozdov [31] relax this assumption, but the distinction in these approaches between 'reacted' and 'unreacted' Li in the solid does not have a clear physical interpretation.

Here, we suggest that Li insertion into Si is accompanied by an irreversible, dissipative transformation of the underlying Si network, and that models of Li-Si based on the Larche–Cahn theory of transport in solids must be modified in order to take this into account. The transformation of crystalline Si to an amorphous structure upon Li insertion is clear evidence that irreversible changes in Si structure occur at least during the first lithiation cycle. There is good reason to believe that similar atomic-scale rearrangements must occur even in amorphous Si. These changes in Si structure have several consequences. Firstly, the free energy of stress free Li-Si is no longer only a function of concentration, but also of the atomic structure. At the same time, the atomic structure is not uniquely determined by composition, but is dependent on the history of electrochemical and mechanical loading. This is the case for all solids, of course, but it is usually assumed that the atomic structure will adopt its minimum energy configuration over time-scales that are very short compared to those associated with transport, and that the structural contribution to free energy is negligible to the chemical binding energy. At least the first of these, and quite possibly the second, is not true for Li-Si. Secondly, transport in amorphous Si is known to be highly sensitive to its atomic structure. The Li diffusion coefficient in Li-Si is therefore likely to evolve with its atomic structure and may be history dependent. Thirdly, changes in the Li-Si structure are likely to result in a volume change. This implies that stresses will play a role in driving the structural changes, and in turn, the structural changes will alter the mechanical behavior of Li-Si alloys. This provides a mechanistic explanation for the coupling between the Li insertion reaction that is captured by recent 'reactive flow' models.

Our goal in this paper is therefore to extend the Larche–Cahn model of diffusion in stressed solids to account for irreversible changes in the atomic structure that occur concurrently with diffusion. The extensions are relatively minor. Like Larche and Cahn, we assume that diffusion in Li-Si takes place by discrete atomic jumps on a fixed (but randomly structured) lattice network, in which some sites are unoccupied. The lattice structure can deform under stress. We merely extend this picture by allowing the number of potential sites that can be occupied by Si in the solid to vary. New unoccupied sites can be nucleated by a thermally activated process, driven by the appropriate thermodynamic driving force (which includes a contribution from stress). If the number of vacant sites exceeds the equilibrium concentration, the same process allows excess sites to be annihilated. In addition, we assume that plastic shear deformation induced by mechanical stresses that exceed the flow stress will nucleate additional vacancies, by disrupting the underlying atomic structure.

We describe this idealization in more detail in the following section; and outline a set of thermodynamically consistent constitutive equations that might characterize the processes of interest. The qualitative predictions of this model are discussed and compared with previous models in Section 3. Conclusions, and possible future extensions of the model are discussed in Section 4.

2. Model

Our model follows closely the description of equilibrium and transport in multi-component elastic solids proposed by Larche and Cahn [32,33], with two important extensions. In the original Larche Cahn model, diffusion takes place by exchange of atoms

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