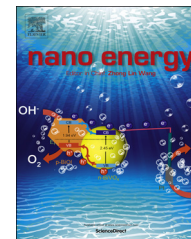




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RAPID COMMUNICATION

Brittle versus ductile fracture mechanism transition in amorphous lithiated silicon: From intrinsic nanoscale cavitation to shear banding



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Abstract

Large-scale atomistic simulations were performed to investigate the fracture behaviors of amorphous lithiated silicon. The simulation results revealed that as the lithium concentration increases, there exists a transition in fracture mechanism from intrinsic nanoscale cavitation to extensive shear banding ahead of the crack tip. It is shown that the observed fracture-mechanism transition can be understood from the changing ratio between critical stresses for cavitation and plastic yield under increasing lithium content. Furthermore, we investigated the mechanistic details of cavitation (i.e. growth of nanovoids) in amorphous lithiated silicon using fully three-dimensional atomistic simulations. It was revealed that in a low lithium concentration environment, an initial void grows heterogeneously by merging with neighboring nucleated voids. However, at high lithium concentrations, the initial void continues to grow in a homogeneous mode. These atomistic mechanisms provide a fundamental understanding of how silicon anodes in lithium-ion batteries fracture during lithiation. © 2015 Elsevier Ltd. All rights reserved.

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Introduction

Lithium-ion batteries have found increasingly broad applications in portable devices, power tools and electric vehicles, owing to its high energy density and long cycle life [1], and silicon has been identified as a promising negative electrode material for lithium-ion batteries due to its exceptional theoretical charge capacity of 4200 mAh/g, which is about 10 times higher than that of the conventional graphite anodes [2]. However, the large volume changes of silicon during lithiation and delithiation can lead to rapid capacity fading during electrochemical cycling due to the fracture induced by loss of electrical contact between active materials and accumulation of solid electrolyte interphase (SEI) layers [2-4].

So far, numerous studies have been aimed to understand the deformation and fracture behaviors of lithiated silicon electrodes [3,7-20]. Experiments on lithiation of silicon nanoparticles have shown that the particle diameter and crack size are two important length scales for fracture, and that there exists a critical particle size of ~ 150 nm, below which there is no fracture and above which surface cracking occurs [7]. Various nanostructured silicon electrodes in the forms of nanopillars, nanowires, nanofilms and nanoporous structures have been proposed to take advantage of the enhanced material resistance to fracture at nanoscale [2-10]. A vast majority of experimental, computational and theoretical studies [11-19] have confirmed that lithiated silicon electrodes can deform plastically. A combination of in-situ uniaxial tensile tests inside a transmission electron microscope (TEM) and ab-initio calculations on lithiated silicon nanowires [9] has shown that the axial tensile strength can be reduced by 80 percent from pristine silicon to lithiated $\text{Li}_{15}\text{Si}_4$ alloy, while the fracture strain doubles, suggesting that lithiated silicon can deform plastically even at the nanoscale [9]. Recently, Pharr et al. reported that the measured fracture energy of lithiated silicon thin-film electrodes is essentially independent of lithium concentration [21], which is apparently inconsistent with the fact that lithiated silicon can deform plastically and plastic deformation should enhance the fracture energy of a material. The above studies highlight the need for a fundamental study on the underlying mechanism of fracture in lithiated silicon. To address this need, here we use large-scale molecular dynamics (MD) simulations to analyze the influence of lithium concentration on fracture behaviors in amorphous lithiated silicon (a- Li_xSi).

Methods

The simulations were performed based on LAMMPS [22]. Five types of lithiated silicon were constructed with different lithium concentrations of $x=0.33, 1.00, 1.71, 3.25$ and 4.40 . We first randomly inserted a specific concentration of lithium atoms into the tetrahedral sites in a crystalline silicon lattice, and then imposed a melting-and-quenching process [23] on the Li-Si mixture to ensure an amorphous structure of the final sample. In the melting-and-quenching process, the temperature was allowed to rise gradually from 1 K to 2500 K within a relaxation time of 300 ps, and then cooled down to 1 K with a rapid cooling rate of about 6 K/ps. For comparison, we also prepared two amorphous samples of pure silicon and pure

lithium through the same thermal treatments from silicon and lithium single crystals, respectively. All simulated samples had the same dimension of $200 \times 122 \times 2$ nm³, consisting of about 3.1 million atoms. A sharp edge crack with length of 60 nm was introduced in the middle of the samples by preventing atomic interaction across the crack surfaces. The cracked samples were then subjected to mode I stretching with a constant strain rate of 5×10^8 s⁻¹ according to the method given in Ref. [23]. During loading, periodic boundary condition was imposed in the thickness direction of the samples, and the temperature was maintained at 1 K via Nose-Hoover thermostat [24]. The atomic interactions were described by a modified embedded atom method (MEAM) potential [25,26]. This potential can predict the mechanical properties of both crystalline and amorphous LiSi alloys, such as the elastic moduli, the compositional expansion, the diffusivity of Li, and the yield strength [26], with results in good agreement with those from experimental measurements and ab-initio calculations [26].

Results and discussion

Figure 1a-g shows a series of snapshots of crack propagation in the simulated samples of amorphous a- Li_xSi . In samples with relatively low lithium concentrations (i.e. $x \leq 1.71$), nanosized voids spontaneously nucleate ahead of the crack tip, then gradually grow and eventually coalesce with the main crack, as illustrated in Figure 1a-d. The coalescence of these nanovoids leads to fast crack propagation with tiny corrugations on the crack surfaces. Nanoscale void nucleation, growth and coalescence have been observed in metallic glasses [23,27,28] and proposed as a typical mechanism responsible for brittle fracture in amorphous materials [23]. In contrast, for samples with sufficiently high lithium concentrations (i.e. $x \geq 3.25$), no cavitation is observed throughout the simulations, rather some shear bands are seen to form near the crack tip at about $\pm 45^\circ$ with respect to the crack, as shown in Figure 1e-g. As the applied strain increases, the crack tip becomes blunted due to extensive shear banding around the crack tip. This is especially prominent in the extreme case of amorphous lithium (a-Li). In contrast to samples with low lithium concentrations, those with high lithium concentrations undergo large amounts of plastic deformation (accommodated by shear banding), leading to large plastic zones near the crack tip. These phenomena indicate that samples with sufficiently high lithium concentrations should fracture in a ductile mode. The simulation results shown in Figure 1 indicate that as the lithium concentration increases, there should be a brittle-to-ductile transition in lithiated silicon at a critical lithium concentration, due to a switching of fracture mechanism from brittle fracture via nanoscale void nucleation, growth and coalescence with the main crack to ductile fracture via extensive shear banding at the crack tip.

Our simulations show that spontaneous cavitation ahead of the crack tip is a controlling mechanism responsible for brittle fracture in lithiated silicon at relatively low lithium concentrations. To understand why cavitation only occurs in samples with low lithium concentrations, we investigated the critical hydrostatic stress for spontaneous void nucleation, referred to as the cavitation stress σ_c . For a given lithium concentration, we selected different sample sizes from 0.48 nm to 18 nm, and for each selected size, we

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