Journal of the Mechanics and Physics of Solids 000 (2017) 1–18

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Crack growth and fracture toughness of amorphous Li-Si anodes: Mechanisms and role of charging/discharging studied by atomistic simulations

S.M. Khosrownejad*, W.A. Curtin

Laboratory for Multiscale Mechanics Modeling, EPFL, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 31 March 2017
Revised 6 June 2017
Accepted 21 June 2017
Available online xxx

Keywords:
Lithium-ion battery
Silicon anode
Fracture
Discharging
Delithiation

ABSTRACT

Fracture is the main cause of degradation and capacity fading in lithiated silicon during cycling. Experiments on the fracture of lithiated silicon show conflicting results, and so mechanistic models can help interpret experiments and guide component design. Here, large-scale K-controlled atomistic simulations of crack propagation (R-curve K_I vs. Δa) are performed at Li_xSi compositions $x = 0.5,\ 1.0,\ 1.5$ for as-quenched/relaxed samples and at $x = 0.5,\ 1.0$ for samples created by discharging from higher Li compositions. In all cases, the fracture mechanism is void nucleation, growth, and coalescence. In as-quenched materials, with increasing Li content the plastic flow stress and elastic moduli decrease but void nucleation and growth happen at smaller stress, so that the initial fracture toughness $K_{Ic} \approx 1.0MPa\sqrt{m}$ decreases slightly but the initial fracture energy $J_{Ic} \approx 10.5J/m^2$ is similar. After $10\,nm$ of crack growth, the fracture toughnesses increase and become similar at $K_{Ic} \approx 1.9MPa\sqrt{m}$ across all compositions. Plane-strain equi-biaxial expansion simulations of uncracked samples provide complementary information on void nucleation and growth. The simulations are interpreted within the framework of Gurson model for ductile fracture, which predicts $J_{Ic} = \alpha\sigma_y D$ where $\alpha \simeq 1$ and D is the void spacing, and good agreement is found. In spite of flowing plastically, the fracture toughness of Li_xSi is low because voids nucleate within nano-sized distances ahead of the crack ($D \approx 1nm$). Scaling simulation results to experimental conditions, reasonable agreement with experimentally-estimated fracture toughnesses is obtained. The discharging process facilitates void nucleation but decreases the flow stress (as shown previously), leading to *enhanced* fracture toughness at all levels of crack growth. Therefore, the fracture behavior of lithiated silicon at a given composition is not a material property but instead depends on the history of charging/discharging. These findings indicate that the mechanical behavior (flow and fracture) of lithiated Si must be interpreted within a fully rate- and history-dependent framework.

1. Introduction

Silicon is among the highest Li-storing anode materials in Li-ion batteries, making it attractive for applications. However, the large capacity is accompanied by significant volume expansion that causes mechanical failure. Crystalline Si also

* Corresponding author.
E-mail address: mostafa.khosrownejad@epfl.ch (S.M. Khosrownejad).

http://dx.doi.org/10.1016/j.jmps.2017.06.010
0022-5096/

amorphizes during the first *Li* charging cycle, so that the operative material is an amorphous $Li-Si$ system that can flow plastically at high stresses. Understanding the *Li* diffusion, volume expansion, plastic flow, and fracture of amorphous lithiated silicon is thus a major area of current research.

Recent experimental studies have been performed on the fracture of lithiated silicon, with conflicting results. Pharr et al. (2013) indirectly measured the in-situ fracture energy of lithiated silicon thin-film electrodes as a function of lithium concentration. Many electrodes were placed in an electrochemical cell and charged and discharged simultaneously. At discrete *Li* concentration levels, individual electrodes were disconnected and the sizes of any cracks formed were measured. Using the measured thin film stress and the standard model for steady-state thin-film crack growth Beuth (1992), an upper bound for the fracture energy was reported to be relatively small ($5-15 J/m^2$), for a material that can flow plastically, and nearly independent of *Li* content. Wang et al. (2015) performed cube-corner indentation cracking tests on thin-film Li_xSi lithiated silicon electrodes. Load and crack size were then used to estimate fracture toughness; note that this method is well-established to be only semi-quantitative Quinn and Bradt (2007). Cracks were observed at moderate loads for *Li* content $x=0$ to $x=1.09$ with fracture toughness increasing with increasing *Li* content. For $x=1.56$, however, no cracking was observed up to high loads, indicating high damage tolerance, and thus suggesting very high fracture toughness although the method does not permit any calculation of fracture toughness. The results of Wang et al. and Pharr et al. are similar in magnitude at low *Li*, $0<x<1$, although with differing trends, and differ significantly at higher *Li* content. Since neither experiment is a clean measure of the fracture toughness, and since the loading conditions in the two experiments are very different, the mechanisms and fundamental material fracture toughness of Li_xSi versus composition x remain uncertain.

The difficulty and inconsistency of the experimental studies motivate the theory and simulation of this problem. Wang and Chew (2016) simulated porosity evolution within Li_xSi over a range of compositions using molecular dynamics method and reported changes in patterns of bond breaking. Similarly, Wang et al. (2015) performed very small scale MD simulations of fracture in Li_xSi alloys to study bond breaking in front of crack. Such studies are probably insufficient for understanding either fracture mechanisms or fracture energy. Ding et al. (2015) performed large-scale single-edge crack tension atomistic simulations and reported a change in fracture mechanism from the void formation at low lithium Li_xSi to shear banding for high lithium Li_xSi. However, a small single-edge cracked specimen requires high loads, driving plasticity far from the crack that is not related to the fracture process, making it difficult to quantify fracture energies. Here, we apply systematic large-scale, K-controlled molecular dynamics simulations to study fracture in lithiated silicon versus composition and charging/discharging history. We study initiation and propagation up to10′s of *nm* of crack growth under small-scale yielding conditions that allow for the measurement of fracture resistance curves and fracture toughness. We study as-quenched materials that correspond to "well-relaxed" material (within the limitations of MD time scales) and materials that have been quenched to composition x_∞ and then discharged to a lower composition, which leads to excess stored energy relative to the "well-relaxed" material and reduced yield stress (see Khosrownejad and Curtin (2016)). Trends in behavior with composition and discharge history are examined. In general, we find the fracture toughness to be low, $K_{Ic}\simeq 1MPa\sqrt{m}$ and $J_{Ic}\simeq 10J/m^2$, comparable to experiments after adjustment for the yield stress difference. Finding the mechanism to be void nucleation, growth, and coalescence, we perform simulations of plane-strain expansion to help corroborate the evolution of voids observed ahead of the crack tip as a function of alloy composition. We then analyze our results in terms of the Gurson model for ductile fracture, which provides insights and a quantitative framework for the problem. The Gurson model predicts $J_{Ic}=\alpha\sigma_y D$, $\alpha\simeq 1$, and the measured low toughness is thus due to the fact that the void nucleation distance D is on the scale of 1 *nm*. The resistance curve behavior is also consistent with the Gurson model. For discharged materials, the yield stress is lower but the void nucleation distance D is larger, leading to higher fracture toughness and fracture energy for all amounts of crack growth studied. The fracture energy remains small, and application of the Gurson model with α and D from simulations again shows consistency with experimental fracture energies.

The remainder of this paper is organized as follows. We review the theoretical background on ductile fracture in Section 2. The simulation details for K-controlled fracture tests are described in Section 3. Results for as-quenched samples are presented and discussed in Section 4. Plane-strain biaxial tension tests are described and presented in Section 4.3. Finally, we discuss the results for the K-controlled fracture tests for discharged samples and analyze them in Section 5 and discuss the relation between our result and experiments in Section 6.

2. Review of ductile fracture theory

Fracture can be viewed equally in terms of energy or stress-intensity, and here we consider both. In mode I plane strain conditions, the relation between mechanical energy release rate J_I and the applied stress intensity factor K_I is

$$J_I = \frac{(1-\nu^2)K_I^2}{E} \tag{1}$$

Irwin suggested that a crack advances in an elastoplastic solid when the energy release rate J_I equals the crack growth resistance Γ_I

$$J_I = \Gamma_I(\Delta a) \tag{2}$$

The crack resistance is a function of the amount of crack growth Δa, and $\Gamma_I(\Delta a)$ usually increases with increasing Δa due to an increasing plastic zone around the crack. The goal of material fracture modeling is to understand the mechanisms and evolution of the material resistance Γ_I.

Please cite this article as: S.M. Khosrownejad, W.A. Curtin, Crack growth and fracture toughness of amorphous Li-Si anodes: Mechanisms and role of charging/discharging studied by atomistic simulations, Journal of the Mechanics and Physics of Solids (2017), http://dx.doi.org/10.1016/j.jmps.2017.06.010