

Fracture Toughness of Li_xSi Alloys in Lithium Ion Battery

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Abstract:

A fundamental understanding of the fracture toughness of the Li_xSi alloys is crucial for the rational design of Si based high-capacity and failure-resistant electrodes. In this study, molecular dynamics (MD) simulation informed continuum chemo-mechanical modelings with integration algorithm of the classic Rice's J-integral were conducted to derive the fracture toughness of Li_xSi alloys. Our modeling results, which are reasonably consistent with the limited publication results derived from different experimental measurements, revealed that the fracture toughness of Li_xSi alloys with low lithium concentration is not sensitive to the lithium concentration. In addition, we demonstrated that, if lithium redistribution caused by the stress gradient around crack tip need to be considered, an appropriate chemo-mechanical path-independent J-integral needed to be used as the classic Rice's J-integral is path-dependent. The obtained fracture toughness of

the Li_xSi alloys provides guidance for the rational design of Si based electrodes, and the approach presented here also sheds light for the evaluation of the fracture toughness of energy materials at different charging/discharging level.

Keywords:

Lithium ion battery; Li_xSi alloy; molecular dynamics simulation; chemo-mechanical model; fracture toughness; lithium redistribution

1. Introduction

Lithium (Li) ion batteries (LIBs), due to their high energy density, have been dominantly used as power sources in portable electronics.¹⁻⁴ However, the relative low capacity of currently commercialized LIBs has seriously hindered their extensive application in some emerging applications, such as electric vehicles and large energy grid.⁵⁻

⁷ It is well-known that silicon (Si) stands as a most promising anode material owing to its highest theoretical capacity (4200 mAh/g).⁸⁻¹⁰ Nevertheless, Li insertion/extraction during charging/discharging cyclings will inherently induce huge volumetric change and stress inside the Si anode, leading to fracture, pulverization, electrical disconnectivity, and ultimately capacity loss.¹¹⁻¹⁸ Therefore, a fundamental understanding of the degradation mechanisms in the Si anode during lithiation/delithiation cycling, especially the mechanics of damage initiation and propagation in the Si anode, is crucial for the rational design of

next-generation failure-resistant Si based electrodes.

Recent experimental studies evidenced that crystalline Si (*c*-Si) undergoes ~300% volumetric change during lithiation/delithiation cycling, leading to the fracture of Si nano-particles even in the first lithiation cycle when the particle size is larger than ~150 nm.^{11, 15-16, 19} For amorphous Si (*a*-Si), the volumetric change is ~280%.²⁰⁻²¹ However, the critical fracture size of *a*-Si particles can increase to ~870 nm.²⁰ In order to investigate the fracture behavior of lithiated Si, Pharr *et al.* estimated the fracture energy of lithiated Si thin film by measuring the curvature changes of the film at different lithiation and delithiation stages, concluding that the fracture energy of lithiated Si is almost independent of lithium concentration as the obtained fracture toughness is $8.5 \pm 4.3 \text{ J/m}^2$ at low lithium concentration ($\sim \text{Li}_{0.7}\text{Si}$) and has the bounds of $5.4 \pm 2.2 \text{ J/m}^2$ to $6.9 \pm 1.9 \text{ J/m}^2$ at high concentration ($\sim \text{Li}_{2.8}\text{Si}$).²² However, the nanoindentation based measurements conducted by Wang *et al.* revealed a highly lithium concentration dependent fracture behavior of lithiated Si, namely, with the increment of lithium concentration, the fracture toughness first decreases from $2.85 \pm 0.15 \text{ J/m}^2$ for unlithiated *a*-Si to a minimum value at $\text{Li}_{0.31}\text{Si}$, and then increases substantially, reaching to $8.54 \pm 0.72 \text{ J/m}^2$ for $\text{Li}_{1.09}\text{Si}$, which indicates a brittle-to-ductile transition of fracture with the increase of lithium concentration in Si.²³ In consideration of the discrepancy between these two experimental studies, it is worthwhile to further investigate of the fracture toughness of Li_xSi as it ultimately dictates the cyclability of Si based electrodes.

Previous works have demonstrated that molecular dynamics (MD) simulation can

be adopted as an appropriate method to computationally assess the fracture properties of materials.²⁴⁻²⁸ For instance, a perfect match was found between the MD simulation results and experimental data for crystalline Si structures, indicating that MD simulation is capable to calculate the fracture toughness.²⁴⁻²⁶ However, as the lithiated Li_xSi can undergo relatively large plastic deformation before fracture failure compared with unlithiated Si, attentions should be paid to the large scale yielding around crack tip when calculating fracture toughness.²⁹⁻³² Therefore, in this study, a MD simulation informed continuum chemo-mechanical model is presented for the calculation of fracture toughness of Li_xSi alloys. In particular, MD simulations are conducted for the material properties of Li_xSi alloys (i.e., Young's modulus, Poisson's ratio, and yield stress) and the critical fracture strain under which the crack in the pre-cracked specimen starts to propagate. Based on the obtained material properties and critical fracture strain, a continuum chemo-mechanical model is used to calculate the stress distribution in the same cracked specimen with the critical strain loading. With the stress distribution information, J-integral is directly calculated for fracture toughness.

2. Methodology

2.1. MD simulation

In our MD simulation, the newly developed second nearest-neighbor modified embedded atom method interatomic potential (2NN MEAM) of Li-Si alloy is adopted to account for the interactions among Li and Si atoms.³³⁻³⁴ This 2NN-MEAM interatomic

potential of Li-Si alloy has been adequately demonstrated to provide the primary properties and lattice structures of both crystalline and amorphous Li_xSi alloy successfully.³³ Based on this potential, MD simulations are conducted for the material properties of Li_xSi alloys and the critical fracture strain under which the crack in the pre-cracked specimen starts to propagate.

The atomic structures of different Li_xSi alloys are created by melting-quenching method.³⁵ First, large enough pure *c*-Si block is generated by using LAMMPS MD simulator. Second, according to the ratio x between the number of Li atoms and Si atoms of different Li_xSi alloys, Li atoms are randomly inserted into the Si block for corresponding compositions. Then, with periodic boundary conditions (PBC) prescribed in all three directions of the simulation cell and the time step set to be 1 fs, the temperature of the Li_xSi block is increased from 0 K to 2500 K during the first 100 ps, and maintained there for another 400 ps, and finally decreased to 10 K with quenching rate 5.0 K/ps during the following 500 ps. Finally, the obtained fully amorphized Li_xSi block is relaxed for 500 ps using NPT ensemble.

To understand the mechanical behaviors of Li_xSi alloys, MD simulations at 10 K are conducted to obtain the uniaxial tensile stress-strain relationships. Columns ($30 \times 30 \times 80$ Å) are cut from the fully relaxed Li_xSi blocks. Tensile simulations with NPT ensemble are carried out by applying a constant strain rate (5×10^7 1/s) along the axial direction of the columns. In addition, PBCs are prescribed in all three directions of the simulation box and the pressure on the surfaces normal to the loading direction is relaxed to zero to ensure

the deformation of the columns is uniaxial. Based on the obtained stress-strain curves, the mechanical properties of Li_xSi alloys, such as Young's modulus and yield stress, are estimated.

For the study of the fracture behaviors of Li_xSi alloys, simulation cells with the size of $500 \times 350 \times 15 \text{ \AA}$ in x , y , and z directions are cut from the fully relaxed Li_xSi blocks. PBCs are applied in both y and z directions. An edge crack with $90 \text{ \AA}$ initial length and $4 \text{ \AA}$ width in XY plane is created in the middle of the cell along x direction, as illustrated in Figure 1(a). After fully relaxed, the cell is stretched in y direction by changing the length of simulation box with a constant strain rate $5 \times 10^7 \text{ 1/s}$. All the MD simulations are conducted at 10 K in LAMMPS with 1 fs time step. The stress and strain at the critical moment that the crack starts to propagate are recorded for the next step chemo-mechanical calculations.

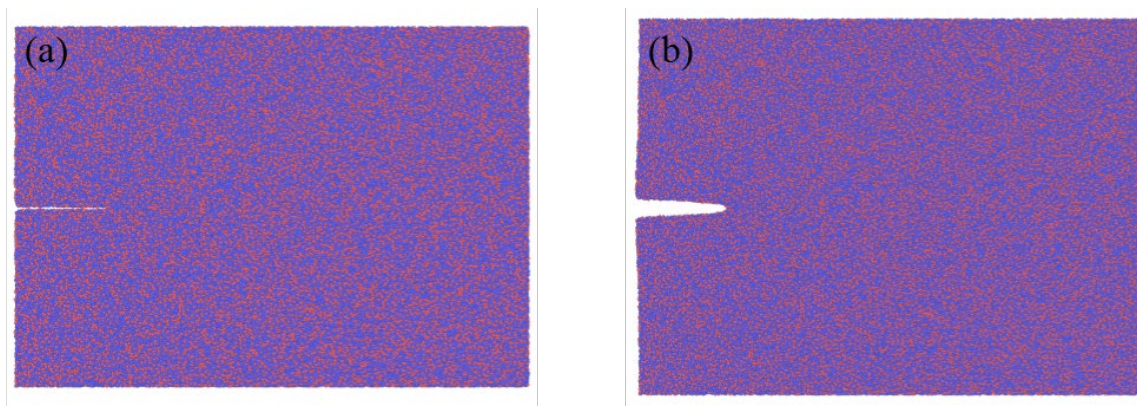


Figure 1. A typical Li_xSi alloy cell for MD simulation with a pre-existed edge crack. (a) Initially, the size of the simulation cell is about 500 , 350 , and $15 \text{ \AA}$ in x , y , and z dimension, respectively. Initially, the crack is about $90 \text{ \AA}$ in length and $4 \text{ \AA}$ in width direction. (b)

Configuration of the simulation cell at the critical moment that the crack starts to propagate.

2.2. Chemo-mechanical simulation

The previously developed finite strain chemo-mechanical model is adopted in this study.^{18, 32, 36} In this model, the concurrent chemical reaction and diffusion processes are simulated in a unified manner by a non-linear diffusion model, despite the difference in interfacial reaction and bulk diffusion. Therefore, the classical diffusion equation is used to describe Li transport in the Si:

$$\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{J}_F, \quad \mathbf{J}_F = -D \nabla \mu, \quad (1)$$

where, c is the Li concentration, D is a diffusion constant, $\mathbf{J}_F$ is the Li flux that related to the chemical potential of Li, μ , in Si defined as follows:³⁷

$$\mu = \mu_0 + R_g T \log \frac{c}{c_{\max} - c} - V_m \eta \sigma_{kk}. \quad (2)$$

The $\mu_0 + R_g T \log \frac{c}{c_{\max} - c}$ and $V_m \eta \sigma_{kk}$ are the stress-independent and stress-dependent parts of the chemical potential, respectively. μ_0 is a constant representing the chemical potential at a standard state, R_g is the gas constant, $c_{\max}$ is the concentration corresponding to the saturation state, V_m is the molar volume, η is the coefficient of compositional expansion, and σ_{kk} is the trace of stress tensor. For the mechanics part of the model, the finite-strain elasto-plastic framework is used, in which the total stretch rate tensor $\mathbf{d}$ is decomposed into three additive parts:

$$\mathbf{d} = \mathbf{d}^e + \mathbf{d}^p + \mathbf{d}^c, \quad (3)$$

where, $\mathbf{d}^e$, $\mathbf{d}^p$, and $\mathbf{d}^c$ are the elastic, plastic, and chemical stretch rates, respectively.

With the same sized edge cracked Li_xSi samples as used in above MD simulation, the following equilibrium equation

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad (4)$$

is solved with corresponding boundary conditions. All the material properties obtained from the above MD simulations, such as Young's modulus, Poisson's ratio, and yield stress, are adopted as inputs for the modeling. Using the implicit coupled temperature-displacement procedure in ABAQUS/Standard with user subroutines, the corresponding Li concentration and stress-strain fields are updated incrementally. Meanwhile, contour integrations are conducted for both the classic Rice's J-integral.³⁸

$$J_\Gamma = \int_{\Gamma_2} (W_e n_i - t_i \frac{\partial u_i}{\partial x_1}) d\Gamma \quad (5)$$

where, as shown in Figure 2, t_i is the traction vector on the contour $\partial\Omega$ that around the crack tip, n_i is the unit outward normal on $\partial\Omega$, u_i is the displacement vector, $d\Gamma$ is the length element along the contour, and W_e is the elastic energy density.

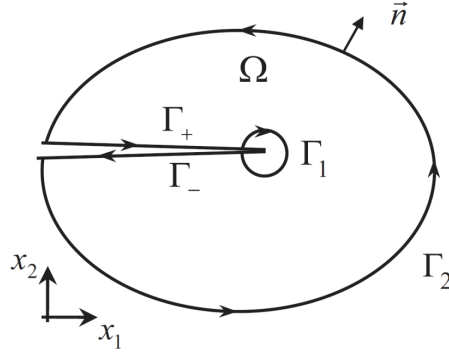


Figure 2. A crack tip contour used in the J-integral calculation. The planar crack is oriented along the x_1 direction, the region Ω around the crack tip is surrounded by the closed contour $\partial\Omega = \Gamma_1 + \Gamma_- + \Gamma_2 + \Gamma_+$, and $\mathbf{n}$ the unit outward normal on $\partial\Omega$.

3. Results and discussion

Upon successfully setting the simulation cell and corresponding boundary and loading conditions, uniaxial tensile simulations of Li_xSi samples, such as crystalline $\langle 111 \rangle$ -Si, a -Si, a - $\text{Li}_{0.25}\text{Si}$, a - $\text{Li}_{0.50}\text{Si}$, a - $\text{Li}_{0.75}\text{Si}$, and a - $\text{Li}_{1.00}\text{Si}$, are conducted at 10 K under the strain rate of 5×10^7 1/s. For the amorphous Li_xSi samples, eight different configurations are simulated for each compositional case to average the obtained results. As shown in Figure 3, the obtained stress-strain curves of a - Li_xSi exhibit the typical characteristics of metallic materials.³⁵ Material properties of pure Si and Li_xSi alloys, such as Young's modulus and yield stress, are estimated from the stress-strain curves. As listed in the Table 1, the Young's modulus and yield stress of Li_xSi alloys are highly dependent on the concentration of Li, while the Poisson's ratio is non-sensitive to the variation of Li concentration.

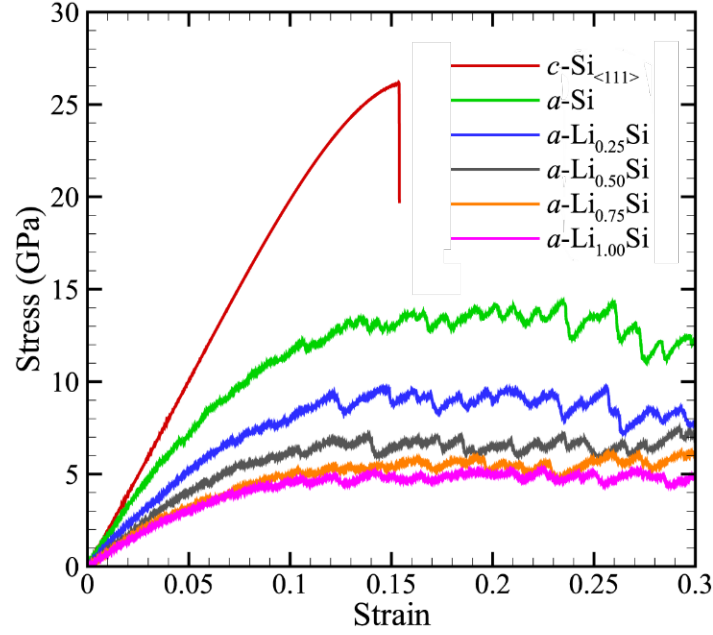


Figure 3. Uniaxial tensile stress-strain curves of crystalline $\langle 111 \rangle$ -Si, α -Si, and α -Li_xSi at 10 K under the strain rate of 5×10^7 1/s .

MD simulations of pre-cracked pure Si and Li_xSi alloy samples are conducted at 10 K to investigate their fracture behavior. During the simulation, interaction between the two pre-exist crack surface is shield. Under the constant strain rate loading condition, the crack tip open displacement increases gradually. With the increment of Li concentration in the Li_xSi alloy samples, much blunter crack tip can be observed. At the critical moment that the crack starts to propagate, as shown in Figure 1(b) as an example, the critical strain is recorded and listed in Table 2. It should be noted that, as all the MD simulation are conducted with an extremely high strain rate (5×10^7 1/s), the simulation time is too short for Li migration. Therefore, no Li redistribution around crack tip is observed, even though

previous studies have already demonstrated that Li atoms are highly mobile and can easily be driven by stress gradient.³⁹⁻⁴⁵

Table 1. The Young's modulus (E), Poisson's ratio (ν), and yield stress (σ_Y) of pure Si and Li_xSi alloys obtained from the uniaxial tensile simulations.

	E (GPa)	ν	σ_Y (GPa)
<111>-Si	189.4	0.17	11.7
α -Si	151.7	0.27	6.7
α -Li _{0.25} Si	105.6	0.33	5.4
α -Li _{0.50} Si	82.8	0.35	4.1
α -Li _{0.75} Si	70.8	0.37	2.9
α -Li _{1.00} Si	65.9	0.34	2.7

Using the material properties obtained in the above MD simulations as inputs, continuum level chemo-mechanical calculations are conducted for the fracture toughness of pure Si and Li_xSi alloys. The same sized pre-cracked 2D plane strain samples are used, and the corresponding critical strain is applied as boundary conditions. As no Li redistribution is observed in the above MD simulations, Li distribution in the samples is assumed to be uniform throughout the chemo-mechanical simulation. Therefore, for simplicity of the model, no Li transport need to be considered in the chemo-mechanical modeling. As a demonstration of the method presented in this study, we first calculated the fracture toughness of <111>-Si as $J_C = 3.60 \text{ J/m}^2$ based on the contour integration of the

classic Rice's J-integral, leading to the critical stress intensity factor as

$K_{IC<111>} = \sqrt{J_C \frac{E}{1-\nu^2}} = 0.84 \text{ MPa}\sqrt{\text{m}}$, which is in a good agreement with the reported experimental measurements, namely $K_{IC} = 0.83 \sim 0.95 \text{ MPa}\sqrt{\text{m}}$.⁴⁶⁻⁴⁷ This calculation indicates that the approach presented here is appropriate for the derivation of fracture toughness. With confidence about the method, we next calculate the fracture toughness of *a*-Si and Li_xSi alloys, as listed in Table 2. The obtained fracture toughness for the low lithium concentration cases investigated in this study matches the experimental results published by Pharr *et al* quite well.²² In addition, with the increment of Li concentration in the Li_xSi alloys, the fracture toughness decreases first to a minimum value around Li_{0.25}Si and then increases. This trend agrees well with the previous experimental measurement conducted by Wang *et al*.²³

It should be noted that, as high strain rate is used in the above study, Li transport during the chemo-mechanical calculation of fracture toughness can be neglected. However, in reality, the loading time scale in quasi-static fracture toughness measurements is comparable to the Li diffusion time scale.⁴³ Therefore, it is important to consider the Li redistribution caused by the stress gradient around the crack tip.⁴⁵

Table 2. The critical strain and fracture toughness (J_C) of pure Si and Li_xSi alloys obtained from MD simulation and chemo-mechanical modeling, respectively.

	Critical strain	J_C (J/m ²)
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$\langle 111 \rangle$ -Si	0.0245	3.60
α -Si	0.0341	5.80
α -Li _{0.25} Si	0.0363	4.73
α -Li _{0.50} Si	0.0441	5.39
α -Li _{0.75} Si	0.0449	5.29
α -Li _{1.00} Si	0.0450	4.80

As shown in Figure 4, without considering Li transport considered, Li distribution (b) is uniform in the sample, and the classic Rice's J-integral (c) obtained from three different integration contours are overlapping with each other, indicating that the J-integral is path-independent. However, with the same far field stress loading conditions, the crack tip stress gradient can drive Li to aggregate around the crack tip (e) when the Li transport is considered, causing more severe stress concentration in the effective stress (d). In addition, Li concentration gradient around the crack tip can lead to the path-dependent behavior of the classic Rice's J-integral, as shown in Figure 4(f).

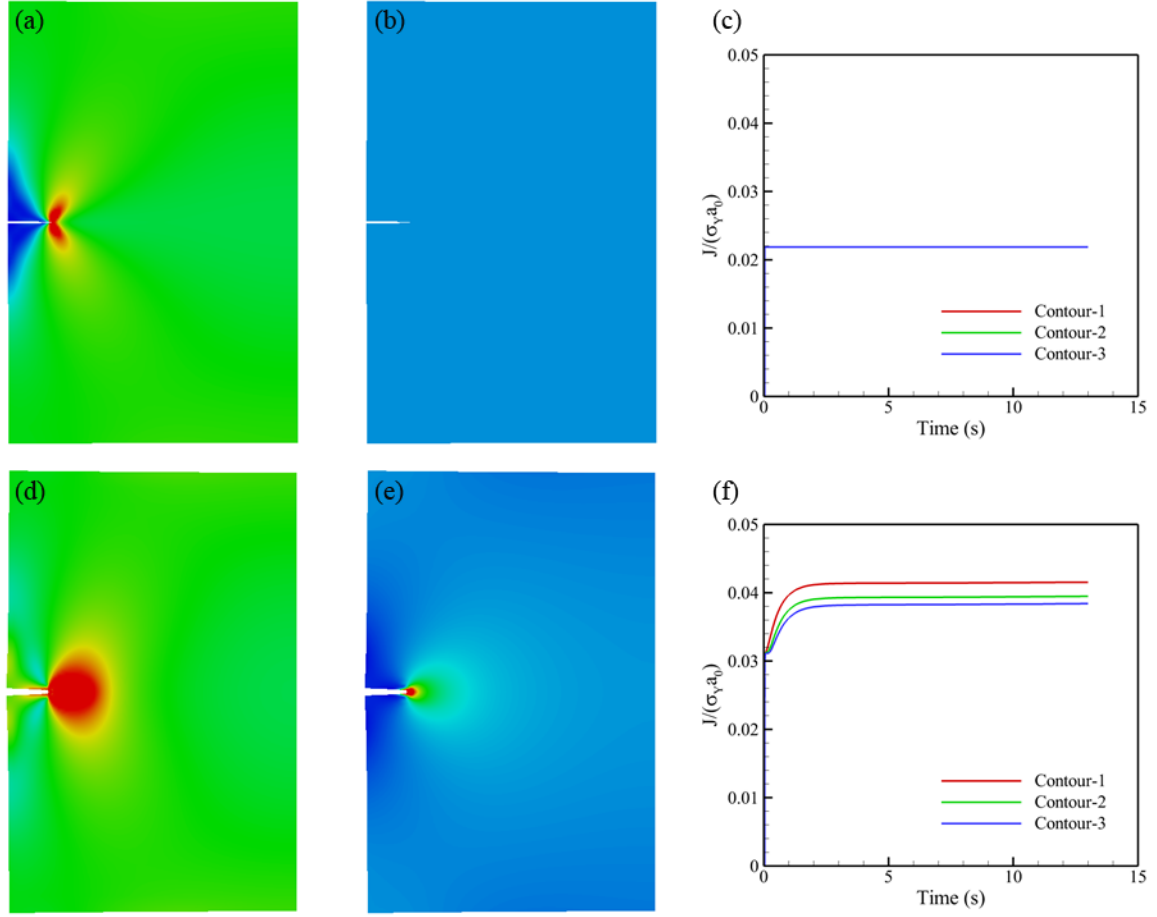


Figure 4. Compared with the effective stress (a), Li concentration (b), and normalized J-integral (c) obtained from the case without Li transport, under the same far field stress loading conditions, the crack tip stress gradient can drive Li to aggregate around the crack tip (e), causing more severe stress concentration in the effective stress (d), and leading to the path-dependent behavior of the classic Rice's J-integral (f).

In order to overcome the limitation of the classic Rice's J-integral when there exist Li concentration gradient, the newly developed chemo-mechanical J-integral need to be used for the calculation of fracture toughness.³⁷ The chemo-mechanical J-integral is

defined by:

$$J_{\Gamma}^{cm} = \int_{\Gamma_2} (\psi n_1 - t_i \frac{\partial u_i}{\partial x_1}) d\Gamma, \quad \psi = W_e - (\mu - \mu_0)c - TS, \quad (6)$$

where, T is the absolute temperature, and S is the entropy of mixing per volume of mixture giving by:

$$S = -R_g c_{\max} \left[\frac{c}{c_{\max}} \log\left(\frac{c}{c_{\max}}\right) + \left(1 - \frac{c}{c_{\max}}\right) \log\left(1 - \frac{c}{c_{\max}}\right) \right]. \quad (7)$$

Using this chemo-mechanical J-integral, the fracture toughness for the case with Li transport is calculated, as shown in Figure 5. With the Li flow caused by crack tip stress gradient, the chemo-mechanical J-integrals obtained from different integration contours differ slightly from each other. Once the Li redistribution reaches a steady state, the chemo-mechanical J-integrals will finally converge a single value, indicating the path-independent property of this chemo-mechanical J-integral.

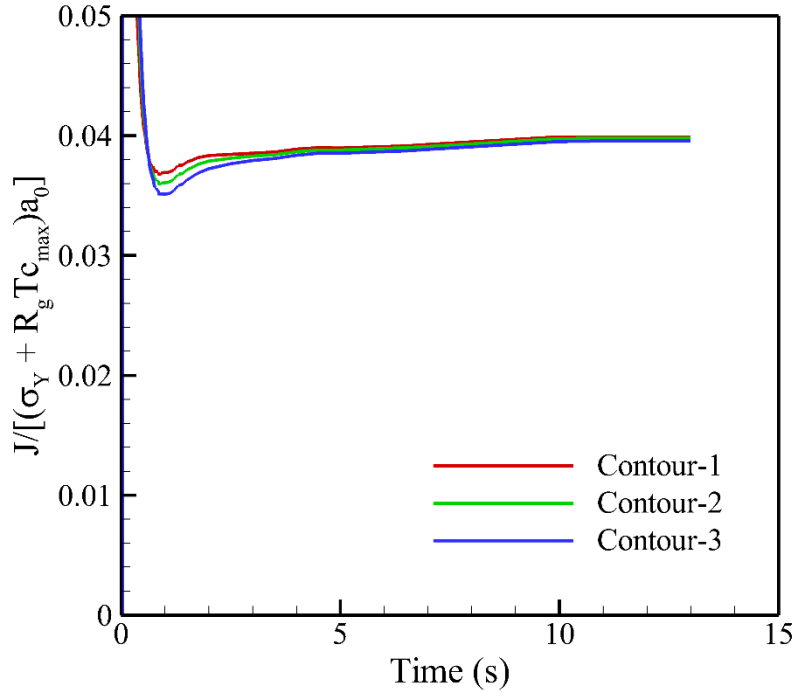


Figure 5. Chemo-mechanical J-integrals obtained from different integration contours. With the Li flow caused by crack tip stress gradient, the chemo-mechanical J-integrals obtained from different integration contours differ slightly from each other. Once the Li redistribution reaches a steady state, the chemo-mechanical J-integrals will finally converge a single value, indicating the path-independent property of this chemo-mechanical J-integral.

4. Conclusions

In conclusion, we have presented a molecular dynamics (MD) simulation informed continuum chemo-mechanical model with integration algorithm of the classic Rice's J-integral for the investigation of the fracture toughness of Li_xSi alloys. In this model, MD simulations are used to calculate the material properties and the critical fracture strain of Li_xSi alloys. Using the obtained MD simulation results as inputs, continuum level chemo-mechanical simulations are conducted for the stress field and fracture toughness of Li_xSi samples with small scale yield.

Using the presented model, we investigated the fracture toughness of Li_xSi alloys with low Li concentration. Our modeling results, which are reasonably consistent with the limited published results derived from different experimental measurements, revealed that the fracture toughness of Li_xSi alloys with low Li concentration is not sensitive to the lithium concentration. In addition, we demonstrated that, when the loading time scale of fracture test is comparable to the Li diffusion time scale, Li redistribution caused by the

stress gradient around crack tip need to be considered, as stress gradient can drive Li to migrate from the far field to crack tip, generating a Li concentration there, and this process is both thermodynamically and kinetically favorable. Under such circumstance, the classic Rice's J-integral turns into path-dependent. Therefore, an appropriate chemo-mechanical path-independent J-integral needed to be used for the calculation of fracture toughness. The obtained fracture toughness of the Li_xSi alloys provides guidance for the rational design of Si based electrodes, and the approach presented here also sheds light for the evaluation of the fracture toughness of energy materials at different charging/discharging level.

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