External Proposals Submitted/Awarded as a Result of ISEN Funding

Proposal: An Interatomic Potential for LixSi Alloys and Its Applications to Lithiation Induced Deformation and Failure in Silicon - Submitted to NSF-CMMI, October 1, 2011 (pending).

Publications and Presentations Resulting From ISEN Funding

1. Publications

(1) Zhiwei Cui, Feng Gao and Jianmin Qu, A finite deformation stress-dependent chemical potential and its applications to lithium-ion batteries, *Journal of the Mechanics and Physics of Solids*, 2011 (under review).

(2) Zhiwei Cui, Feng Gao, Zhihua Cui and Jianmin Qu, Developing a second nearest-neighbor modified embedded atom method interatomic potential for lithium, *Modelling and Simulation in Materials Science and Engineering*, 2011 (accepted for publication).


2. Presentations

(1) Deformation and stresses during lithium insertion in silicon, *NU TAM seminar*, Northwestern University, March, 2011

(2) Stress-dependent chemical potentials and their applications to energy conversion and storage devices (invited), *The 3rd International Conference on Heterogeneous Materials Mechanics (ICHMM2011)*, Shanghai, China, May, 2011.


Summary of Research

Under ISEN support, we have

1. Developed the second nearest-neighbor embedded atom method (2NN-MEAM) interatomic potentials for Li-Li, Si-Si and Li-Si, with the aid of particle swarm optimization (PSO) and first-principles calculations.
2. Calculated the materials properties of amorphous Li-Si alloys by using the developed 2NN-MEAM interatomic potentials. These material proprieties were used as inputs to the continuum models.
3. Extended our previous continuum models to account for fully two-way stress-diffusion coupling, finite strain and plastic deformation during lithiation into Si anode.

Details of above results are presented below.

1. 2NN-MEAM interatomic potential development

Silicon (Si) is being considered as a promising anode material owing to its highest known theoretical charge capacity (4200 mAh/g)[1]. However, the volume expansion of the initial Si can be as much as 400% after fully charged, which always leads to poor cyclic ability. The mechanics the damage initiation and propagation during lithiation into Si anode has not been fully understood yet. A key roadblock is the insufficient material database for Li-Si amorphous alloys, which are usually formed during lithiation. There are very few experimental results associated with the Li insertion into Si anode. The ab initio approach is accurate whereas time-consuming. For the large-scale model simulation, such as atoms diffusion and crack initiation and propagation, molecular dynamics (MD) method is preferred, assuming an accurate and robust interatomic potential is available to describe the atomic interactions. Currently, only the modified embedded atom method (MEAM) interatomic potential proposed initially by Baskes, can be applied for fcc, bcc, hcp, diamond and molecular materials by using the same formalism[2]. Later on, Lee et al. extended the original MEAM to second nearest neighbor MEAM (2NN MEAM) by accounting for the interactions of 2NN neighbors to heal the flaws arising from the original MEAM ones[3].

In a 2NN MEAM formulation, the total energy of a system is written as [3]

\[ E = \sum_i \left[ F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(i)} \varphi_{ij}(R_{ij}) \right], \]

where \( F_i \) is the embedding function, \( \bar{\rho}_i \) is the background electron density at the site where atom \( i \) occupies, and \( \varphi_{ij}(R_{ij}) \) is the pair interaction between atoms \( i \) and \( j \) at a
distance $R_{ij}$. We used the particle swarm optimization (PSO) method \cite{4} to determine simultaneously all the unknown parameters in the 2NN MEAM potential, which has been widely adopted in many areas such as power system, structural damage identification, nonlinear system identification, ice-storage air conditioning system, etc. The PSO method starts with a group (called swarm) of candidate solutions (called particles). These particles move around within the search space to seek food (called optimum). Let $\Pi(j)$ be an objective function that transforms a particle to a unique real number. The goal is to find a particular particle $j$ such that $\Pi(j) \leq \Pi(k)$ for all particle $k$ within the search space. The results are depicted in Tables 1 and 2.

Table 1 Optimized parameters in the 2NN MEAM potential for Li and Si. The units of the cohesive energy $E_c$ and equilibrium nearest neighbor distance $r_e$ are in eV and Å, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$E_c$</th>
<th>$r_e$</th>
<th>$\alpha$</th>
<th>$d$</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$\beta^{(2)}$</th>
<th>$\beta^{(3)}$</th>
<th>$t^{(1)}$</th>
<th>$t^{(2)}$</th>
<th>$t^{(3)}$</th>
<th>$C_{\text{max}}$</th>
<th>$C_{\text{min}}$</th>
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<td>Li</td>
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<td>2.99</td>
<td>3.00</td>
<td>0.14</td>
<td>0.64 1.03</td>
<td>4.88</td>
<td>4.15</td>
<td>5.27</td>
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<td>4.13</td>
<td>0.57</td>
<td>1.91</td>
<td>0.31</td>
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<tr>
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<td>4.92</td>
<td>0.07</td>
<td>0.39 2.35</td>
<td>2.35</td>
<td>2.51</td>
<td>0.00</td>
<td>3.07</td>
<td>3.89</td>
<td>9.08</td>
<td>2.55</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 1 Optimized parameters in the 2NN MEAM potential for Li-Si alloys.

<table>
<thead>
<tr>
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<th>$E_c$</th>
<th>$r_e$</th>
<th>$\alpha$</th>
<th>$d$</th>
<th>$C_{\text{max}}$</th>
<th>$C_{\text{max}}$</th>
<th>$C_{\text{max}}$</th>
<th>$C_{\text{min}}$</th>
<th>$C_{\text{min}}$</th>
<th>$C_{\text{min}}$</th>
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<th>$\rho_0$</th>
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<td>1.61</td>
<td>1.71</td>
<td>2.07</td>
<td>0.50</td>
<td>0.29</td>
<td>0.51</td>
<td>0.88</td>
</tr>
<tr>
<td>-Si</td>
<td>0</td>
<td>9</td>
<td>8</td>
<td>0</td>
<td>2.76</td>
<td>1.61</td>
<td>1.71</td>
<td>2.07</td>
<td>0.50</td>
<td>0.29</td>
<td>0.51</td>
<td>0.88</td>
</tr>
</tbody>
</table>

2. Material properties calculation by molecular dynamics

The amorphization will take place at the very early stage of lithiation into Si anode, thus the amorphous Li-Si alloys must be considered carefully for the mechanics assessment. Our developed 2NN-MEAM interatomic potential for Li-Si alloys is anticipated to play an important role to determine the materials properties of amorphous Li-Si alloys. Shown in Figure 1a is the generated Li$_3$Si$_1$ amorphous structure by using the developed 2NN-MEAM interatomic potentials. The radial distribution function (RDF) profiles were also calculated, as shown in Figure 1b. Our results are in perfect agreement with the ones by \textit{ab initio} approach, indicating the reliability of the developed interatomic potentials for Li-Si alloys.
It has been demonstrated that the mean square displacement (MSD) increases linearly with time when diffusion occurs, and the slope of the MSD vs. time curve gives the diffusion constant $D$. However, at lower concentration level, it is not readily to calculate the diffusivity due to the unstable MSD trend at room temperature. Therefore, we tried to extract the diffusivity by extrapolating the results obtained at high temperatures through the following Arrhenius equation.

As seen in Figure 2, the diffusivity of Li in amorphous Li$_x$Si alloy is greater than that of Si by an order of magnitude, indicating that Li is the dominant diffusion species. Furthermore, the diffusivity of Li is orders of magnitude smaller in crystalline Li$_x$Si than that in the corresponding amorphous alloy. The vastly difference in diffusivity between amorphous and crystalline structures may be a major cause of the observed radial cracking of Si particles and wires[5].
Shown in Figure 3a are the extracted stress-strain curves from MD simulation results for amorphous Li$_x$Si, which is subjected to a uniaxial loading under the strain rate of $10^8$ at 300K. A clear plastic deformation occurs even at such high strain rate. And an ideal elastic-plastic constitutive relation is suggested for all the amorphous Li$_x$Si alloys studied here. The yield strength of the alloys is then readily to be extracted from the stress-strain curves, as shown in Figure 3b. It can be seen that the yield strength decreases dramatically with increasing of Li concentration in Li$_x$Si. It is striking that the yield strength shows strong dependence on the applied strain rate. Generally, a higher strain rate leads to higher yield strength.

3. **Extension of continuum numerical model**

Based on the previous numerical model developed by PI, an extended framework was established by accounting for the finite strain and plastic deformation during lithiation. The total deformation can be viewed as a sequence of eigen-transformation represented by $F^r$ followed by an elastic deformation represented by $F^e$, as illustrated in Figure 4.

As an example to illustrate the application of this new stress-dependent chemical potential, the stress fields in a spherical amorphous Si particle induced by Li insertion/extraction are investigated in both elastic and elastic-plastic regimes. In the elastic regime, we showed that the critical particle size is inversely related to the insertion rate and scales up as a power law function of the yield strength, see Figure 5a. In the elastic-plastic regime, we found that the hoop stress becomes positive during charging, indicating the particle surface is subjected to tensile hoop stress. We postulated that this tensile hoop stress near the particle surface is responsible for the radial cracks observed in experiments[5].

![Figure 3 (a) Uniaxial stress-strain curves of amorphous Li$_x$Si alloys at 300K under the strain rate of $10^8$; and (b) Yield strength as a function of Li concentration in amorphous Li$_x$Si alloys under different strain rates.](image1)

![Figure 4. Decomposition of the total deformation.](image2)
Figure 5 (a) Critical particle size against plastic deformation as a function of charging rate; and (b) Evolution of hoop stress at the particle surface. The inserts are to show the behavior at short charging time.

References