

## Inelastic hosts as electrodes for high-capacity lithium-ion batteries

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Silicon can host a large amount of lithium, making it a promising electrode for high-capacity lithium-ion batteries. Upon absorbing lithium, silicon swells several times its volume; the deformation often induces large stresses and pulverizes silicon. Recent experiments, however, indicate that under certain conditions lithiation causes inelastic deformation. This paper models such an inelastic host of lithium by considering diffusion, elastic-plastic deformation, and fracture. The model shows that fracture is averted for a small and soft host—an inelastic host of a small feature size and low yield strength. © 2011 American Institute of Physics. [doi:10.1063/1.3525990]

Lithium-ion batteries are the batteries of choice for diverse applications, especially for those sensitive to size and weight, such as portable electronics and electric cars.<sup>1</sup> Intense efforts are being made to develop lithium-ion batteries of high capacity, fast charging, and long life.<sup>2–4</sup> When the battery is charged and discharged, the electrode absorbs or desorbs lithium, inducing cyclic deformation and possibly fracture—a mechanism known to cause the capacity of the battery to fade.<sup>5</sup>

Lithiation-induced deformation and fracture is a bottleneck in developing lithium-ion batteries of high capacity. For example, of all known materials for anodes, silicon offers the highest theoretical specific capacity.<sup>3</sup> Still, silicon is not used in anodes in commercial lithium-ion batteries, mainly because after a small number of cycles the capacity of silicon fades, often attributed to lithiation-induced fracture.<sup>6</sup>

Recent experiments, however, have shown that the capacity can be maintained over many cycles for silicon anodes of small feature sizes, such as nanowires,<sup>3</sup> thin films,<sup>7</sup> and porous structures.<sup>8</sup> For such anodes lithiation-induced strain can be accommodated by inelastic deformation. For instance, cyclic lithiation causes silicon thin films and silicon nanowires to develop undulations.<sup>3,7</sup> Furthermore, the stress in a silicon thin film bonded on a wafer has been measured showing that the film deforms plastically upon reaching a yield strength.<sup>9</sup>

Existing models of lithiation-induced deformation and fracture have assumed that the electrodes are elastic.<sup>10–18</sup>

Here, we model inelastic electrodes by considering diffusion, elastic-plastic deformation, and fracture. The model shows that fracture is averted for a small and soft host of lithium—an inelastic host of a small feature size and low yield strength.

We classify hosts of lithium into two types: elastic and inelastic. For an elastic host, the host atoms recover their configurations after cycles of charge and discharge [Fig. 1(a)]. For example, for an electrode of a layered structure, lithium diffuses in the plane between the layers, leaving the strong bonds within each layer intact. Elastic hosts are used

in commercial lithium-ion batteries for both cathodes (e.g., LiCoO<sub>2</sub>) and anodes (e.g., graphite). By contrast, an inelastic host does not fully recover its structure after cycles [Fig. 1(b)]. For example, when an electrode is an amorphous solid, such as amorphous silicon, the host atoms may change neighbors after a cycle of charge and discharge.

Whether lithiation-induced strain will cause an electrode to fracture depends on the feature size of the electrode.<sup>5,15–18</sup> The energy release rate  $G$  for a crack in a body takes the form  $G = Z\sigma^2 h/E$ , where  $h$  is the feature size,  $E$  Young's modulus,  $\sigma$  a representative stress and  $Z$  a dimensionless number of order unity.<sup>19</sup> Fracture is averted if  $G$  is below the fracture energy of the material,  $\Gamma$ . Consequently, fracture is averted if the feature size is below the critical value

$$h_c = \frac{\Gamma E}{Z\sigma^2}. \quad (1)$$

Representative values for silicon are  $\Gamma = 10 \text{ J/m}^2$  and  $E = 80 \text{ GPa}$ .<sup>20</sup>

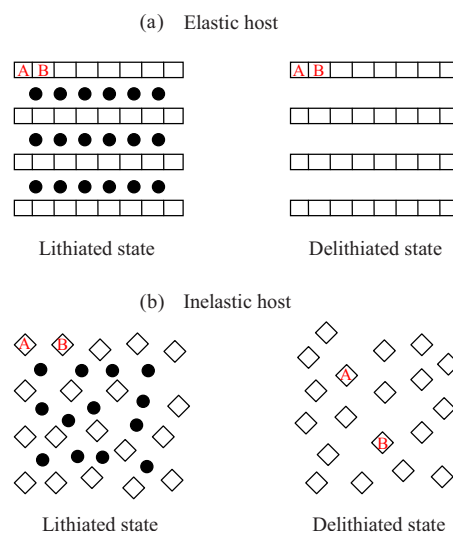


FIG. 1. (Color online) (a) For an elastic host of lithium, the host atoms recover their configurations after a cycle of lithiation. (b) For an inelastic host of lithium, the host atoms may change neighbors after a cycle of lithiation. Squares represent host atoms and circles represent lithium atoms.

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If silicon were an elastic host, the lithiation-induced strain  $\varepsilon=100\%$  would cause stress on the order  $\sigma\sim E\varepsilon$ . Equation (1) would predict a subatomic critical size.<sup>21</sup> This prediction disagrees with the experimental observations—silicon anodes of feature sizes around 100 nm do survive many cycles of charge and discharge without fracture.<sup>3,7</sup>

By contrast, for an inelastic host, lithiation-induced strain can be accommodated by inelastic deformation. For a thin film of silicon bonded on a thick substrate, the measured yield strength is  $\sigma_Y=1.75$  GPa.<sup>9</sup> For a channel crack in the film,  $Z=2$  is a typical value.<sup>19</sup> Using these values, Eq. (1) predicts a critical thickness of 130 nm. This prediction agrees well with available experimental observations: a 250 nm silicon thin film fractured after a few cycles,<sup>22</sup> while a 50 nm silicon film survived without fractures after 1000 cycles.<sup>7</sup> In general, for an inelastic electrode of a large capacity, fracture is averted if the feature size is small and the yield strength is low. One extreme is a liquid electrode, which accommodates the absorption-induced strain by flow, and can potentially provide ultrahigh capacity.<sup>23</sup>

During charge and discharge, the stress in an electrode is a time-dependent field. Furthermore, the magnitude of the stress may exceed the yield strength at places under triaxial constraint. We describe an inelastic host of lithium by adapting an elastic and perfectly plastic model. The increment of the strain is taken to be the sum of three contributions

$$d\varepsilon_{ij} = d\varepsilon_{ij}^e + d\varepsilon_{ij}^p + d\varepsilon_{ij}^l, \quad (2)$$

where  $\varepsilon_{ij}^e$  is the elastic strain,  $\varepsilon_{ij}^p$  the plastic strain, and  $\varepsilon_{ij}^l$  the lithiation-induced strain. Hooke's law gives

$$d\varepsilon_{ij}^e = d \left\{ \frac{1}{E} [(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] \right\}, \quad (3)$$

where  $\nu$  is Poisson's ratio.  $\delta_{ij}=1$  when  $i=j$  and  $\delta_{ij}=0$  otherwise.  $J_2$ -flow rule gives

$$d\varepsilon_{ij}^p = \begin{cases} 0, & \sigma_e < \sigma_Y \\ 0, & \sigma_e = \sigma_Y, \quad d\sigma_e < d\sigma_Y \\ \lambda s_{ij}, & \sigma_e = \sigma_Y, \quad d\sigma_e = d\sigma_Y \end{cases}, \quad (4)$$

where  $s_{ij} = \sigma_{ij} - \sigma_{kk}\delta_{ij}/3$  is the deviatoric stress and  $\sigma_e = \sqrt{3s_{ij}s_{ij}}/2$  the equivalent stress. Within the perfectly plastic model,  $\lambda$  at each increment is a positive scalar to be determined by the boundary-value problem. The lithiation-induced strain is proportional to the concentration of lithium

$$d\varepsilon_{ij}^l = d \left( \frac{\beta c}{3} \right) \delta_{ij}, \quad (5)$$

where  $\beta$  is a constant analogous to the coefficient of thermal expansion and  $c$  denotes the normalized lithium concentration in the host.

The concentration of lithium in an electrode is a time-dependent field, taken to be governed by the diffusion equation,  $\partial c / \partial t = D\nabla^2 c$ . For simplicity, here, we assume that the diffusivity  $D$  is a constant and that diffusion is driven by the gradient of concentration alone.

As an illustration of the model, consider a thin film of amorphous silicon bonded on a substrate. Let  $h$  be the thickness of the film, and  $\tau$  the time used to complete charge or

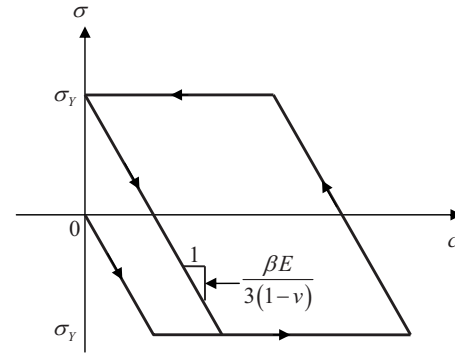


FIG. 2. Evolution of stress in a thin film of an inelastic host during cyclic lithiation and delithiation.

discharge. We consider the limit  $h \ll \sqrt{D\tau}$ , where the film is so thin that the concentration of lithium is homogeneous throughout the thickness of the film. The stresses in the film are given by  $\sigma_{xx} = \sigma_{yy} = \sigma$ ,  $\sigma_{zz} = 0$ , where  $x$  and  $y$  represent the in-plane directions, and  $z$  represents the out-of-plane direction. The in-plane deformation of the thin film is constrained by the substrate, namely,  $d\varepsilon_{xx} = d\varepsilon_{yy} = 0$ . In the elastic stage,

$$\frac{d\sigma}{dc} = - \frac{\beta E}{3(1-\nu)}. \quad (6)$$

Figure 2 plots the stress evolution as a function of lithium concentration  $c$ . Initially, the film deforms elastically and develops a compressive stress, with the slope given by Eq. (6). When the magnitude of compressive stress reaches the yield strength  $\sigma_Y$ , the film deforms plastically. Upon delithiation, the film unloads elastically, develops a tensile stress, and then deforms plastically in tension. The fully lithiated state causes a volume expansion about 300%,<sup>6</sup> so that  $\beta=3$ . For  $\nu=0.22$ .<sup>20</sup> Equation (6) gives the slope  $d\sigma/dc = -103$  GPa, which may be compared to the measured value  $-75$  GPa in Ref. 9.

In the thin film, the stress can be induced by the constraint imposed by the substrate. By contrast, a particle, a nanowire, or a porous structure is almost unconstrained by other materials, and the stress is mainly induced by the inhomogeneous distribution of lithium.<sup>24</sup> Consequently, the stress is small when the feature size and charge rate are small.<sup>11,16,18,24</sup>

To explore the effect of inelastic deformation, we study the evolution of the stress field in a spherical particle of silicon. The particle is initiated as pure silicon, and is charged and discharged at a constant current. The dimensionless charge and discharge rate is set to be  $i_n a / DC_{\max} = 0.206$ , where  $a$  is the radius of the particle,  $i_n$  is the current density for charge and discharge, and  $C_{\max}$  is the theoretical capacity of fully lithiated silicon. This dimensionless rate corresponds to  $i_n = 0.176$  A/m<sup>2</sup> for representative values  $a = 1$   $\mu\text{m}$ ,  $D = 1 \times 10^{-16}$  m<sup>2</sup>/s and  $C_{\max} = 8.52 \times 10^9$  Coulomb/m<sup>3</sup>.

Figure 3(a) and 3(b) show the distribution radial and hoop stresses during charge. As more lithium is inserted, the particle expands more near the surface than near the center, resulting in tensile radial stresses. The hoop stress is compressive near the surface and tensile near the center. For the

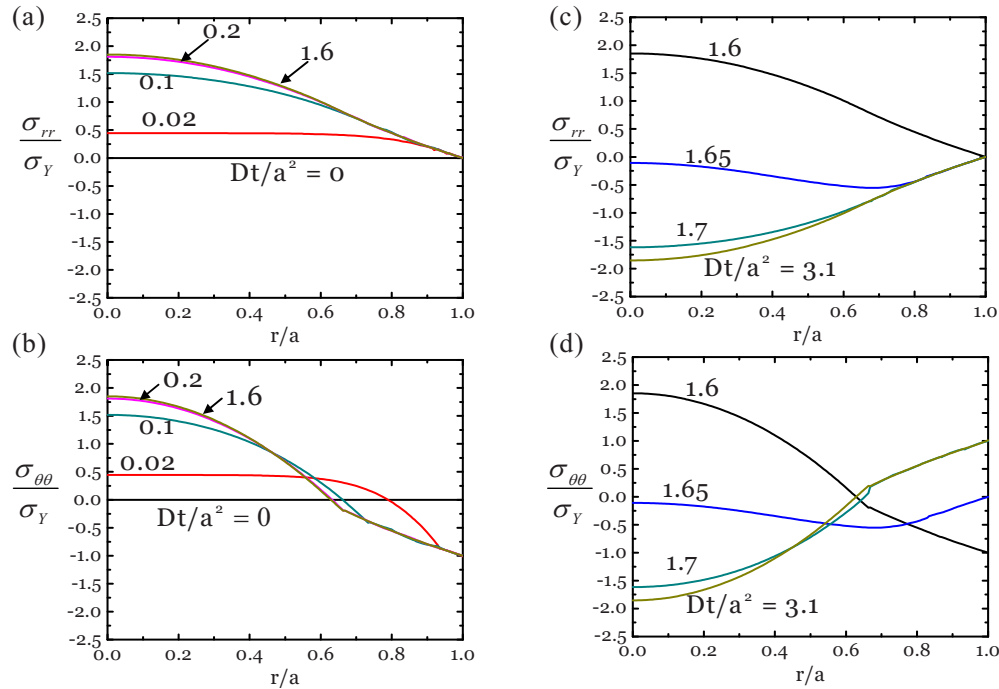


FIG. 3. (Color online) The evolution of (a) radial stress and (b) hoop stress during charge. The evolution of (c) radial stress and (d) hoop stress during discharge.

spherical particle, the yield condition takes the form  $|\sigma_{\theta\theta} - \sigma_{rr}| = \sigma_Y$ . Due to the triaxial constraint at the center, the radial stress and hoop stress can exceed the yield strength. Also, large value of hydrostatic stress may cause an inelastic material to grow cavities.

The lithium concentration at the surface reaches a value of unity at time  $Dt/a^2 = 1.6$ . At this point, we reverse the electric current and start discharge. Figure 3(c) and 3(d) show the distribution of radial and hoop stress during discharge. As lithium desorbs, the radial stress evolves from tension to compression. Also, the hoop stress at the surface becomes tensile with magnitude  $\sigma_Y$ . This tensile stress may result in the propagation of surface flaws.

In summary, we have developed a model of an inelastic host of lithium by considering diffusion, elastic-plastic deformation, and fracture. For an electrode of a small feature size and low yield strength, inelastic deformation can prevent fracture.

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<sup>1</sup>G. A. Nazri and G. Pistoia, *Lithium Batteries: Science and Technology* (Kluwer Academic, Boston, MA, 2003).

<sup>2</sup>Department of Energy, Basic Research Needs for Electrical Energy Storage, 2007.

<sup>3</sup>C. K. Chan, H. L. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, *Nat. Nanotechnol.* **3**, 31 (2008).

<sup>4</sup>B. Kang and G. Ceder, *Nature (London)* **458**, 190 (2009).

<sup>5</sup>R. A. Huggins and W. D. Nix, *Ionics* **6**, 57 (2000).

<sup>6</sup>L. Y. Beaulieu, K. W. Eberman, R. L. Turner, L. J. Krause, and J. R. Dahn, *Electrochem. Solid-State Lett.* **4**, A137 (2001).

<sup>7</sup>T. Takamura, S. Ohara, M. Uehara, J. Suzuki, and K. Sekine, *J. Power Sources* **129**, 96 (2004).

<sup>8</sup>H. Kim, B. Han, J. Choo, and J. Cho, *Angew. Chem., Int. Ed.* **47**, 10151 (2008).

<sup>9</sup>V. A. Sethuraman, M. J. Chon, M. Shimshak, V. Srinivasan, and P. R. Guduru, *J. Power Sources* **195**, 5062 (2010).

<sup>10</sup>R. Deshpande, Y. T. Cheng, and M. W. Verbrugge, *J. Power Sources* **195**, 5081 (2010).

<sup>11</sup>S. Golmon, K. Maute, S.-H. Lee, and M. L. Dunn, *Appl. Phys. Lett.* **97**, 033111 (2010).

<sup>12</sup>H. Haftbaradaran, H. J. Gao, and W. A. Curtin, *Appl. Phys. Lett.* **96**, 091909 (2010).

<sup>13</sup>X. C. Zhang, W. Shyy, and A. M. Sastry, *J. Electrochem. Soc.* **154**, A910 (2007).

<sup>14</sup>J. Christensen and J. Newman, *J. Solid State Electrochem.* **10**, 293 (2006).

<sup>15</sup>Y. H. Hu, X. H. Zhao, and Z. G. Suo, *J. Mater. Res.* **25**, 1007 (2010).

<sup>16</sup>T. K. Bhandakkar and H. J. Gao, *Int. J. Solids Struct.* **47**, 1424 (2010).

<sup>17</sup>K. E. Aifantis, S. A. Hackney, and J. P. Dempsey, *J. Power Sources* **165**, 874 (2007).

<sup>18</sup>W. H. Woodford, Y.-M. Chiang, and W. C. Carter, *J. Electrochem. Soc.* **157**, A1052 (2010).

<sup>19</sup>J. W. Hutchinson and Z. Suo, *Adv. Appl. Mech.* **29**, 63 (1991).

<sup>20</sup>L. B. Freund and S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution* (Cambridge University Press, Cambridge, 2004).

<sup>21</sup>J. Wolfenstine, *J. Power Sources* **79**, 111 (1999).

<sup>22</sup>J. P. Maranchi, A. F. Hepp, A. G. Evans, N. T. Nuhfer, and P. N. Kumta, *J. Electrochem. Soc.* **153**, A1246 (2006).

<sup>23</sup>D. C. Holzman, *New Sci.* **206**, 19 (2010).

<sup>24</sup>K. J. Zhao, M. Pharr, J. J. Vlassak, and Z. G. Suo, *J. Appl. Phys.* **108**, 073517 (2010).