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Size-dependent fracture of Si nanowire battery anodes

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ABSTRACT

We use a unique transmission electron microscope (TEM) technique to show that Si nanowires (NWs) with diameters in the range of a few hundred nanometers can be fully lithiated and delithiated without fracture, in spite of the large volume changes that occur in this process. By analyzing the stresses associated with lithiation and delithiation we conclude that the process does not occur by the growth of discrete crystalline phases; rather it occurs by amorphization of the Si NWs followed by diffusion of Li into the structure. By accounting for the large deformation associated with this process and by including the effects of pressure gradients on the diffusion of Li, we show that Si NWs with diameters less than about 300 nm could not fracture even if pre-existing cracks were present in the NW. These predictions appear to be in good agreement with the experiment.

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1. Introduction

Silicon is one of the most promising anode materials for lithium ion batteries because it has a very high theoretical charging capacity ($\sim$4200 mAh/g). Among various electrode structures tested (Obrovac and Krause, 2007; Kim et al., 2008; Magasinski et al., 2010; Song et al., 2010), silicon nanowires are attractive candidates for electrodes because they provide less constraint on the volume changes that occur during lithium insertion (Chan et al., 2007). A major obstacle to using silicon as an electrode is that it experiences a huge volume expansion – by about 400% – during lithiation/delithiation, which can result in fracture of the nanowires.

A number of models have been developed to deal with this problem. Huggins and Nix (2000) made an initial effort to describe fracture associated with decrepitation during battery cycles using the Griffith criterion in a simple one-dimensional model. Recently, Hu et al. (2010) have used the strain energy release rate as a fracture criteria in two-phase $LiFePO_4/FePO_4$ particles. These models both envisioned lithiation/delithiation as occurring by the growth of discrete Li-rich phases.

To take diffusion of lithium into account, a number of papers have focused on the stresses induced by volumetric strain gradients associated with diffusion. Using the analogy between diffusion and heat flow, diffusion-induced stresses can be modeled as thermal stresses (Prussin, 1961). In models of this type, stresses are generated by the constraints on free expansion, since no stresses develop during free thermal or diffusive expansion. Christensen and Newman (2006a,b) developed a rigorous mathematical model for diffusion-induced stresses and used a critical tensile stress as a fracture criterion. Zhang et al. (2007, 2008) performed detailed numerical simulations of stress evolution in ellipsoidal $LiMn_2O_4$

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Nomenclature

C	concentration [#/nm^3]
C_{max}	maximum lithium concentration [#/nm^3]
D	diffusion coefficient [nm^2/s]
e	unit charge per atom [C/#]
E	Young's modulus [GPa]
i	surface current density [C/(nm^2 s)]
I	total ion current [C/s]
J	mass flux of lithium ion [#/(nm^2 s)]
J_b	surface mass flux of lithium ion [#/(nm^2 s)]
l_x^0	initial length in x direction [nm]
l_y^0	initial length in y direction [nm]
l_z^0	initial length in z direction [nm]
l_x	current length in x direction [nm]
l_y	current length in y direction [nm]
l_z	current length in z direction [nm]
L	length of Si NW [nm]
n_{Li^+}	number of lithium ions inserted [#]
r	radial position [nm]
R	radius of Si NW [nm]
T	temperature [°C]
u	radial displacement [nm]
V_{Si}	volume of Si [nm^3]
V_{final}	final volume [nm^3]
$V_{initial}$	initial volume [nm^3]
$V_{current}$	current volume [nm^3]

Greek

α	extent of lithiation [%]
α_T	thermal expansion coefficient [/°C]
β	stress-diffusion coupling parameter [nm^3]
ε_r	radial strain [·]
ε_θ	tangential strain [·]
ε_z	axial strain [·]
ε_t	transformation strain [·]
ε_{th}	thermal strain [·]
ε_{linear}	linear strain [·]
λ_m	mth zero of 1st order Bessel function of the first kind [·]
ν	Poisson's ratio [·]
ρ	density [g/nm^3]
σ_r	radial stress [GPa]
σ_θ	tangential stress [GPa]
σ_z	axial stress [GPa]
σ_h	hydrostatic stress [GPa]
Ω	partial molar volume of lithium [nm^3/#]

particles and included the effect of pressure gradients on the flux of Li. Verbrugge and Cheng (2008) and Deshpande et al. (2010) derived analytical expressions for the stress evolution during Li diffusion for both the sphere and cylinder geometry and used the tensile stress and strain energy as fracture criteria. Moreover, they Cheng and Verbrugge (2008) suggested that surface tension and modulus could play an important role at the nanometer length scale. Haftbaradaran et al. (2011) have considered various fundamental features of highly nonlinear behavior associated with diffusion at high solute concentrations and compared it with atomistic simulation.

A number of authors have used fracture mechanics to model failure associated with electrochemical shock. Aifantis et al. (2007) have used Griffith's criterion to estimate critical crack size at which cracking will stop. To avoid the assumption of pre-existing cracks, Bhandakkar and Gao (2010) developed a clever cohesive zone model for the nucleation of cracks in a thin strip subjected to diffusion-induced stresses and predicted the critical size below which fracture would be avoided. Woodford et al. (2010) have employed the stress intensity factor to study the growth of a pre-existing dominant flaw in a single-particle electrode. Hu et al. (2010) and Zhao et al. (2010) have also utilized the strain energy release rate as a fracture criterion for electrode particles.

In the present study, we explore two types of models in an effort to obtain insight into the fracture of silicon nanowires subjected to lithiation/delithiation. These modeling results are then directly compared with experiments and they reach a good agreement on the size effect on fracture.

As a first approximation and to illustrate the methodology of our approach, we begin by assuming that discrete phase transformations can occur during the charging/discharging processes, as if a Li_xSi compound exists as an equilibrium phase. Due to the misfit strain between different phases, stresses are generated in order to satisfy mechanical compatibility. However, the stresses using the discrete phase model are much too high for silicon nanowires (Si NWs) to support, and are physically unrealistic, even for the smallest NWs (Beaulieu et al., 2001). Moreover, it has been reported that crystalline silicon quickly transforms to an amorphous phase, when lithium ions diffuse into Si NWs (Limthongkul et al., 2003; Chan et al., 2009). Due to the rapid phase transformation, Li_xSi compounds might not exist as equilibrium phases. When the amorphous phase is formed, diffusion might come into play in the stress evolution. If the lithium ion concentration changes gradually in space, the reason for stress evolution is not the amount of inserted lithium, but rather the lithium concentration gradient. By coupling the stresses to the composition gradients, the stress evolution during lithium ion diffusion may be calculated.

Following the work of many others, we make the analogy between heat transfer and diffusion of matter in order to deal with diffusion-driven deformation (Prussin, 1961; Christensen and Newman, 2006a; Verbrugge and Cheng, 2008; Cheng and Verbrugge, 2008; Deshpande et al., 2010; Bhandakkar and Gao, 2010). However, because the volume expansion is huge, the relationship between the fictitious thermal expansion coefficient and partial molar volume needs to be adjusted to be consistent with large deformation. Moreover, the huge volume expansion and associated pressure can affect the