



Phase-field model for the two-phase lithiation of silicon



Fangliang Gao, Wei Hong*

Department of Aerospace Engineering, Iowa State University, Ames, IA 50011, USA

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ABSTRACT

As an ideal anode material, silicon has the highest lithium-ion capacity in theory, but the broader application is limited by the huge volumetric strain caused by lithium insertion and extraction. To better understand the physical process and to resolve the related reliability issue, enormous efforts have been made. Recent experiments observed sharp reaction fronts in both crystalline and amorphous silicon during the first lithiation half-cycle. Such a concentration profile indicates that the process is likely to be reaction limited. Based on this postulation, a phase-field model is developed and implemented into a finite-element code to simulate the coupled large inelastic deformation and motion of the reaction front in a silicon electrode. In contrast to most existing models, the model treats both volumetric and deviatoric inelastic deformation in silicon as a direct consequence of the lithiation at the reaction front. The amount of deviatoric deformation is determined by using the recently developed kinetic model of stress-induced anisotropic reaction. By considering the role of stress in the lithiation process, this model successfully recovers the self-limiting phenomenon of silicon electrodes, and relates it to the local geometry of electrodes. The model is also used to evaluate the energy-release rate of the surface crack on a spherical electrode, and the result suggests a critical size of silicon nanoparticles to avert fracture. As examples, the morphology evolution of a silicon disk and a Si nanowire during lithiation are also investigated.

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1. Introduction

Lithium (Li) ion batteries have revolutionized the means of energy storage for portable electronics and electric vehicles in the past decades. The demand for even higher energy density has been constantly driving the development of new electrode materials of higher capacity (Armand and Tarascon, 2008). Capable of attaining 4200 mAh g^{-1} in theory (Cui et al., 2012; Obrovac and Christensen, 2004; Weydanz et al., 1999), Silicon (Si) is naturally an attractive candidate of the anode material (Tarascon and Armand, 2001; Goodenough and Kim, 2010; Li et al., 1999; Beaulieu et al., 2001; Limthongkul et al., 2003; Chan et al., 2008; Magasinski et al., 2010). However, the lithiation of Si is usually accompanied by a large volumetric expansion (up to $\sim 270\%$ for fully lithiated Si) (Beaulieu et al., 2001; Obrovac et al., 2004), and the consequent mechanical failure is believed to be the main cause of the capacity deterioration during cycling (Christensen and Newman, 2006; Liu et al., 2011; Lee et al., 2012; Zhao et al., 2012a). The intriguing phenomena in the Li–Si system have recently attracted a large volume of experimental and theoretical studies on the stress development and evolution during lithiation and delithiation processes (Bower et al., 2011; Brassart and Suo, 2013; Christensen and Newman, 2006; Cui et al., 2013; Liu et al., 2011, 2012a; Sethuramana et al., 2010a).

* Corresponding author.

E-mail address: whong@iastate.edu (W. Hong).

During lithiation, at least three processes take place in Si: the electrochemical reaction between Si and Li, the migration of Li, and the elastic and inelastic deformation. The three processes are intrinsically coupled. For example, when a Li ion is migrating through the lithiated Si, each step can be regarded as a lithiation/delithiation reaction. Earlier studies are mostly built upon the coupled Li diffusion and elastic deformation, and focus on the diffusion-induced stress (e.g. Christensen and Newman, 2006; Zhang et al., 2007; Cheng and Verbrugge, 2009; Golmon et al., 2010; DeLuca et al., 2011; Ryu et al., 2011; Grantab and Shenoy, 2012; Haftbaradaran et al., 2010, 2011; Gao and Zhou, 2011). The results have demonstrated the size and rate dependencies of the reaction-induced stress field and the backward effect of stress to the diffusion or reaction rate. It has also been realized that it is impossible for the large volume expansion of Si during lithiation to be accommodated solely by elastic deformation. More recent development of theories often includes the considerations of finite-strain elastic-plastic deformation and reaction kinetics (Bower et al., 2011; Cui et al., 2012, Chen et al., 2014). With the Li migration described as Fickian diffusion, all the aforementioned models would predict a single-phase process, in which Si is lithiated gradually throughout the entire thickness. However, recent experimental observations show that the initial lithiation of Si, either crystalline (c-Si) or amorphous (a-Si), exhibits a two-phase process: the material is divided into the unreacted and the resultant phases by a clear reaction front, through which the Li concentration changes sharply (Limthongkul et al., 2003; Li et al., 2000; Liu et al., 2012a, 2012b; McDowell et al., 2013; Sun et al., 2013; Wang et al., 2013). Similar phenomena are often observed in processes limited by reactions at the interface (Bai and Bazant, 2014). Approaches taken to model the two-phase lithiation of Si include the introduction of a composition-dependent diffusivity with very low value in the unlithiated Si phase (Liu et al., 2011, 2012b), and explicitly addressing the reaction-induced discontinuities at the reaction front (Zhao et al., 2012a; Cui et al., 2013). While both approaches results in the separated phases and related phenomena similar to those observed, the mathematical difficulties such as the numerical stiffness caused by the large difference in time scales and the tracking of moving boundaries have limited the computation to lower dimensions or relatively simple geometries.

Another point of interest in the lithiation process is the inelastic deformation associated with reaction. If Si undergoes isotropic volume expansion during lithiation, the large volume expansion across the reaction front could never be accommodated elastically. An approach often taken is to allow plastic flow in the resultant Li_xSi (and in an intermediate state) when the stress exceeds a critical level, namely the yield strength (Brassart and Suo, 2013; Cui et al., 2013; Chen et al., 2014). However, to match experimental results, the yield strength needs to be taken as composition and kinetics dependent (Brassart and Suo, 2013), and the value is much lower than that of mechanical stress-induced yielding (Zhao et al., 2011). Moreover, recent observations (Pharr et al., 2014) showed a clear dependence of the resultant stress on the rate of lithiation, which does not fit into the existing framework of stress-induced plastic flow. Alternatively, a recently proposed model suggests that the lithiation reaction alone could result in anisotropic inelastic deformation, even when the reacting Si is amorphous (Hong, 2015). Because of the mismatch-induced deviatoric stress, the reaction with anisotropic deformation at certain orientation is experiencing higher driving force and is thus faster. In the process of two-phase lithiation, although the precise nature of the deformation mechanism in the reaction front is less conclusive, the consequence is significant to the stress development in Si anodes. It is evident that: (a) inelastic deformation with finite deviatoric component is present in the resultant immediately after the reaction front, and (b) such inelastic deformation is very different from the conventional defect-mediated plasticity in other materials and in the resultant Li_xSi out of the reaction front.

Built upon the kinetic model of anisotropic reaction (Hong, 2015), this paper abandons plastic flow at the reaction front and seeks an alternative approach to modeling the two-phase lithiation process of Si. By incorporating the kinetic model into a field theory with coupled reaction and elastic deformation, the structural evolution and stress redistribution can be computed in complex geometries. The backward effect of mechanical constraints and stress field to the reaction can also be revealed. To circumvent the difficulty of distinguishing between reaction and diffusion as in the kinetic model (Hong, 2015), the current paper will start by postulating the process to be reaction-limited, and the composition in each phase homogeneous. By using a phase-field method with a scalar phase field varying continuously from the reactant phase (pure Si) to the resultant phase (Li_xSi), the moving reaction front is represented by the transition region with certain characteristic thickness. Phase-field methods are widely used in modeling reaction, phase transition, and morphological evolution (Karma and Rappel, 1998; Boettinger et al., 2002; Chen, 2002). In contrast to the approach of solving the coupled diffusion and elastic-plastic deformation problem (Anand, 2012), which has also been applied in studying Li electrode materials (Di Leo et al., 2014; Chen et al., 2014), here a reaction-limited process is taken to be the starting point, and the phase field variable is used just as a means of tracking the reaction front, similar as that in modeling liquid-phase electrochemical reactions (Guyer et al., 2004a, 2004b).

It should be admitted that the reaction-limited process is only an assumption, which is applicable to relatively small samples or the early lithiation stage of a large sample. Even though the migration of Li in lithiated layer is relatively fast, it will ultimately become the limiting mechanism. In those cases, a fully coupled diffusion-reaction model will have to be used to represent the true physical process.

2. The model

2.1. Phase field for the state of charge

In contrast to the existing models that consider concurrent diffusion and reaction (Brassart and Suo, 2013; Zhao et al.,

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