Modelling stress-affected chemical reactions in non-linear viscoelastic solids with application to lithiation reaction in spherical Si particles

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ARTICLE INFO

ABSTRACT

This paper aims at modelling stress-affected chemical reactions in spherical particles by adopting the chemo-mechanical framework based on the chemical affinity tensor and combining it with the finite-strain non-linear viscoelastic constitutive model. The model is applied to the chemical reaction between lithium (Li) ions and silicon (Si), which has been considered as promising successor to graphite for use as active material in lithium-ion battery (LIB) anodes. However, during charging of LIBs, Si enters into the chemical reaction with Li ions, causing large volumetric expansion of Si particles, which leads to the emergence of mechanical stresses, which, in turn, can affect the kinetics of the chemical reaction even up to the reaction arrest. In this paper, the propagation of the reaction front separating the chemically transformed and the untransformed phases is modelled, and the coupled stress-diffusion-reaction problem is solved using the finite element approach. The model predicts the retardation and the locking of the chemical reaction in Si depending on the values of the chemical energy parameter, which corresponds to experimental observations.

1. Introduction

In recent years, special attention has been paid to the enhancement of the capacity of lithium-ion batteries by investigating the applicability of various active materials, such as silicon, that can accommodate larger amount of lithium atoms than commonly used graphite. The main challenge for the application of Si as a novel anode active material is its large volumetric expansion of up to 300% in the charged state (McDowell, Lee, Nix, & Cui, 2013), which leads to the emergence of the mechanical stress and the degradation/failure of the anode during charge/discharge cycling. Various Si nano-structures such as nanowires, spherical particles embedded into a graphite matrix, porous Si–C composites and special coatings applied to Si particles have been proposed to solve this problem (Lukatskaya, Dunn, & Gogotsi, 2016; Luo, Wu, Luo, Huang, & Dravid,

2014; Magasinski et al., 2010). However, at the moment, there are no straightforward solutions to this problem and deeper understanding of the chemical reaction with Li ions and interaction of Si particles with the surrounding material is required.

From the physical point of view, there is a difference between the mechanism of reaction between Li and graphite and between Li and Si — in the case of graphite, the mechanism is based on the intercalation into the host lattice, while in the case of Si, it is the formation of new chemical compounds ("alloying") (McDowell, Lee, Nix et al., 2013). Thus, the reaction between Li ions and Si can be understood as a chemical transformation. Term "lithiation" of a material is often used in literature to refer to the chemical reaction of the material with Li ions. Therefore, in this paper, the reaction between Li ions and Si is also referred to as the lithiation of Si.

During the initial lithiation (i.e. upon the first cycle) of either crystalline or amorphous Si nano-particles, the existence if two distinct phases, the untransformed and the transformed Si, is observed, while the chemical reaction is localised at the reaction front of nanometre thickness that separates unlithiated and lithiated Si (Cubuk & Kaxiras, 2014; van Havenbergh, Turner, Marx, & van Tendeloo, 2016; Jia & Li, 2015; McDowell, Lee, Harris et al., 2013; McDowell et al., 2012; Yang et al., 2012). This process is referred to as "the two-phase lithiation" in literature. It should be also mentioned that a process, with a smooth change of Li concentration within Si particle (i.e. without a reaction front), was observed upon the subsequent lithiation–delithiation cycles (McDowell, Lee, Harris et al., 2013), which was referred to as "one-phase lithiation". In the case the two-phase process, the lithiation rate is limited by the rate of the chemical reaction taking place at the reaction front. Two modelling concepts of the reaction localisation exist. One type of models deals with a smooth spatial distribution of the lithium concentration and a transition layer with a rapidly changing concentration that connects concentration-poor and concentration-rich phases. For example, in Chen et al. (2014), a phase-field model was proposed and applied to the case of a single spherical Si particle, and lithiation-induced stresses were analysed. Another type of models considers a chemical reaction front as a sharp interface, e.g. Cui, Gao, and Qu (2013) and Jia and Li (2015). In the present paper a sharp reaction front is considered.

The volumetric expansion of Si particles during lithiation leads to mechanical stresses, which influence the kinetics of the reaction between Si and Li. Therefore, from the mechanical perspective, there has been an extensive research focus on modelling of stresses produced by the lithiation, e.g. Dimitrijevic, Aifantis, and Hackl (2012). But the influence of stresses on the lithiation kinetics still remains unclear and must be captured to model the battery charging process accurately. Since Li is delivered to the reaction front by diffusion, stresses may affect the lithiation process via the diffusion flux rate and via the lithiation reaction rate. It should be noted that coupling of stresses, diffusion and chemical reaction has been also intensively discussed in the context of Si oxidation, which is a transformation process of a solid body that is similar to lithiation. In a number of papers, the well-known Deal-Grove model of oxidation (Deal & Grove, 1965) has been modified by considering the classical diffusion equation with the stress-dependent diffusion coefficient and the stress-dependent reaction rate parameter. The choice of stress characteristics (the first invariant, the normal stresses, or the intensity of shear stresses), which affect the reaction and the diffusion parameters, was made intuitively by using the notion of the activation volume, e.g. Kao, McVittie, Nix, and Saraswat (1988), Sutardja and Oldham (1989) and Rafferty (1990). Additionally, a concentration-dependent volumetric expansion was introduced, which led to the total stress-diffusion coupling, e.g. Rao and Hughes (2000) and Rao, Hughes, and Garikipati (2000). A reaction-controlled diffusion model for the lithiation process of a spherical Si particle, in which the reaction front kinetics was modelled as a pressure-dependent process, was proposed in Zhang, Lee, Lee, Cui, and Linder (2015). The influence of stresses on diffusion via additional terms in the diffusion equation in various chemo-mechanical processes has been also considered, e.g. Knyazeva (2003) and Toribio, Kharin, Lorenzo, and Vergara (2011).

Another group of models includes the influence of stresses on the diffusion flux and the chemical reaction rate via a scalar chemical potential, which depends on the concentration and the stresses, and gradient of which governs the flux of the reactant, e.g. Loeffel and Anand (2011), Bower and Guduru (2012); Bower, Guduru, and Sethuraman (2011), Cui, Gao, and Qu (2012), Brassart and Suo (2012, 2013), Levitas and Attariani (2013, 2014), Bower, Guduru, and Chason (2015) and Dal and Miehe (2015). For example, in Dal and Miehe (2015), a stress-diffusion model was presented, in which the isotropic volumetric expansion depends linearly on the concentration of Li, while the diffusion is driven by the spatial gradient of the chemical potential, which is the function of the concentration and the pressure. In Cui et al. (2013), previously developed stress-diffusion model, in which a stress-dependent chemical potential was proposed and applied to the problem of lithiation of a spherical Si particle (Cui et al., 2012), was extended to the problem with a chemical reaction as a kinetics governing process. It should also be mentioned that the velocity of the reaction front can be controlled by the reaction rate at the reaction front rather than by the diffusivity of the reactant (see e.g. Jia & Li, 2015 and reference therein), which is Li ions in the case of lithiation.

The coupled stress-diffusion-reaction models were also extended to describe additional physical effects, such as damage of Si particles upon lithiation. For example, in Zhang, Krischok, and Linder (2016), the approach of Zhang et al. (2015) was extended and the effective damage field was introduced. In Klinsmann, Rosato, Kamlah, and McMeeking (2016a,b), a coupled stress-diffusion model was used to study a crack growth during the lithiation process.

In the present paper, the thermodynamically consistent approach to mechanochemistry of reaction fronts based on the notion of the chemical potential is further developed. In the last decades of the twentieth century it became clear that chemical potentials are tensorial quantities in the case of solid phase transformations, which are related to the Eshelby energy-momentum tensors (see e.g. Grinfeld, 1991 and Abeyaratne & Knowles, 2006 and references therein). This can be explained by the fact that the phase equilibrium takes place at a surface element oriented with respect to the axis of the