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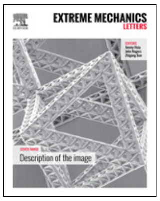

A reaction-controlled diffusion model for the lithiation of silicon in lithium-ion batteries

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ABSTRACT

Silicon is considered as a promising anode material for lithium ion batteries. Despite the great attention on Si anode materials, a consistent description of the diffusion and reaction mechanism at the reaction front of crystalline silicon, amorphous silicon, and delithiated amorphous silicon has not yet been proposed. To better understand those mechanisms, a new reaction-controlled diffusion formulation is proposed. The new formulation makes use of the bond-breaking energy barrier E_0 as the key physical quantity. With the consideration of different values of E_0, the two-phase diffusion during initial lithiation of both crystalline Si and amorphous Si can be well represented with an evident reaction front. In addition, by varying E_0, the one phase lithiation of amorphous Si, obtained after the delithiation process, can be captured with the new formulation. The effect of deformation, hydrostatic pressure at the reaction front, and Li concentration level on the reaction front velocity is taken into account in the proposed model. Numerical simulations are provided to support the model.

1. Introduction

Lithium-ion batteries (LIBs) have become very important energy storage devices due to their high energy density and high average voltage. LIBs with higher energy storage density and longer cycle life are persistently demanded, especially from the emerging electric vehicle industry [1]. Silicon (Si) is a very attractive anode material because of its maximum theoretical specific capacity of up to 4200 mAhg^{-1} and its abundance on earth [2]. However, enormous volume changes (∼310% at full lithiation) caused by the insertion and extraction of Lithium (Li) in Si [3] lead to electrode pulverization and capacity loss [2]. Even though nanotechnology [4] has shed lights on the practical application of Si as the anode material, a thorough understanding of the complicated electro-chemo-mechanical problem involved in the (de)lithiation process of Si is still missing. In particular, further advanced nanomaterial designs, such as those making use of double-walled Si tubes [5], Si-C yolk-shell and pomegranate [6,7], or nanoporous Si [8,9] require such improved mechanical understanding. For an electro-chemo-mechanical coupled model, one important aspect is accurately capturing the Li distribution in Si electrodes resulting from the diffusion and reaction process, which is challenging for existing experiments. More importantly, it is necessary to develop a proper model to describe the Li diffusion during the initial lithiation of crystalline Si (c-Si), amorphous Si (a-Si) and the subsequent lithiation process, which have different diffusion and reaction behaviors, in a consistent manner. To

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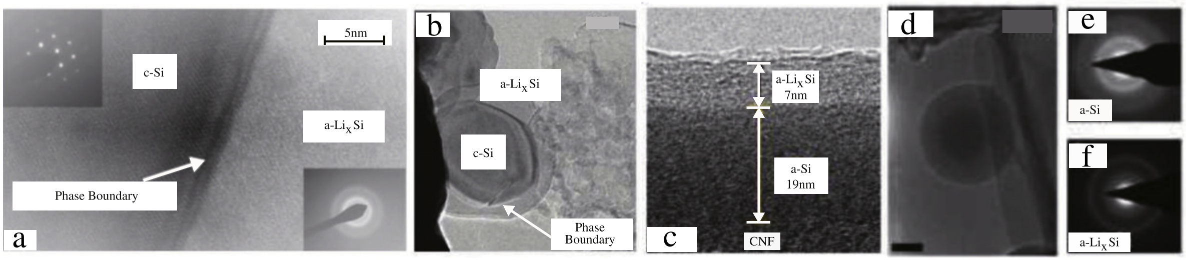

Fig. 1. Experimental observation of the two phase lithiation process in c-Si (a,b) and a-Si (c–f). The a-Li$_x$Si and c-Si (a-Si) form a very sharp phase boundary. (a) Lithiation of c-Si wafer [14], (b) lithiation of c-Si nanoparticle [11], (c) lithiation of a-Si coated on a carbon nanofiber (CNF) [17], (d–f) lithiation of a-Si nanoparticle with the selected area electron diffraction pattern [18].

achieve this, a reaction-controlled diffusion model for the lithiation process of Si is proposed in this work.

During the past few years, thanks to the in situ transmission electron microscopy electrochemical cells technology [10], many interesting features of diffusion processes of Li in Si have been observed. For c-Si, (i) a two-phase diffusion process is reported in [11–13] for the initial lithiation process, as shown in Fig. 1(a,b). As the lithiation proceeds, a layer of amorphous Li-Si alloy (a-Li$_x$Si), the transparent region in Fig. 1(a,b), is produced. The newly formed a-Li$_x$Si and the remaining c-Si forms an evident phase boundary (or reaction front). The lithiated a-Li$_x$Si shell may even crystallize into the Li$_{15}$Si$_4$ phase during lithiation with the presence of a c-Li core [12]. (ii) The reaction front is observed to have a nanoscale thickness with a high Li concentration gradient [14]. (iii) During the initial lithiation of c-Si nanoparticle electrodes, the reaction front is found to slow down as it progresses towards the core [12]. (iv) The initial lithiation of c-Si is anisotropic, resulting in an anisotropic deformation, with a preferred crystal direction $\langle 110 \rangle$ [15,16]. (v) Fracture of c-Si electrodes during the initial lithiation is size dependent, with a critical diameter of ∼150 nm for nanoparticles [11,12].

For a-Si, (i) recent experiments show a similar two phase diffusion process during initial lithiation [17,18], as illustrated in Fig. 1(c–f), where a distinct reaction front can be observed between a-Li$_x$Si and a-Si. However, the Li concentration gradient around the reaction front is not reported in those experiments. (ii) The phase boundary is observed to move at a constant speed [17,18]. (iii) A two-stage lithiation process is postulated in [17] for a-Si where the Li concentration first reaches $x \sim 2.5$ in a-Li$_x$Si, followed by a second lithiation stage when $x \sim 3.75$. (iv) A similar size-dependent fracture phenomenon is observed with a critical diameter of ∼870 nm [18]. As for amorphous Si obtained after the delithiation process (named as "post-a-Si" in this work), a one-phase lithiation is observed in experiments [18].

To capture the aforementioned two-phase diffusion mechanism, a purely empirical concentration-dependent diffusion coefficient is commonly used to describe the sharp Li concentration drop in the lithiation of c-Si electrodes [11,19], where the interfacial reaction is ignored and simply replaced by a non-linear diffusion process. A flexible sigmoid function is also used to create Li profiles with either a sharp phase boundary for two-phase lithiation or a gradually varying concentration for one-phase lithiation in [20] without though modeling the diffusion process as done in this work. The Cahn–Hilliard theory [21] for phase separation also captures the phase transformation from c-Si to a-Li$_x$Si in [22,23], where a concentration gradient dependent interfacial contribution in the free energy formulation is used to describe the interfacial region and to control the interfacial size, but the chemical reaction rate is not taken into account. In [24], the concurrent reaction model for the lithiation of c-Si is proposed, where both the stress and reaction rate are accounted for, but the fact that the stress can stall the reaction in the model does not agree with the fact that the reaction front can be extremely slow but never stops [12]. Also, the model is not able to capture concentration gradients at the sharp interface region, which might be a key factor affecting the reaction-limited diffusion process. Similar as in [24], the competition between chemical reaction and species diffusion is treated by a dimensionless parameter in [25], but accounting for large deformations with the consideration of the reaction front velocity, which is assumed to be constant and is thereby not in line with experimental observations for c-Si [12].

For electrodes considered at the nanoscale, the chemical reaction rate rather than the diffusion itself is the limiting factor for the initial lithiation of c-Si and a-Si [11,12,24,25], whereas the diffusion might be the limiting factor for the one-phase diffusion of post-a-Si [18]. To capture the lithiation process for all three types of Si in a uniform way, a one-way coupling model between the reaction and diffusion is proposed in this work. A physical parameter, the bond-breaking energy barrier, is introduced in this new reaction-controlled diffusion model to investigate the similarities and differences between the initial lithiation process of a-Si and c-Si and the lithiation of post-a-Si. The proposed model will take the effect of Li concentration and hydrostatic pressure at the reaction front on the reaction front velocity into account.

The rest of the paper is organized as follows. Section 2 describes the newly proposed reaction-controlled diffusion model. Several numerical simulations with the consideration of diffusion induced deformation are performed to outline the performance of the proposed model in Section 3. The advantage of the proposed model and its potential applications are discussed in Section 4. Several concluding remarks are given in Section 5.