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A variational framework to model diffusion induced large plastic deformation and phase field fracture during initial two-phase lithiation of silicon electrodes☆

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Highlights

- A variational based computational framework that combines multiple dissipative phenomena is proposed.
- Diffusion induced large plastic deformation and phase field fracture during two-phase lithiation of silicon electrodes is modeled.
- The effect of fracture energy release rate, electrode geometry, and geometric constraints on the fracture behavior of silicon electrodes is investigated.

Abstract

Silicon (Si) is considered to be a promising next-generation anode material for lithium-ion batteries. However, the large volume change during (de)lithiation processes causes fracture of Si electrodes, thereby limiting Si's practical application in lithium-ion batteries. In this work, we formulate a variational-based fully chemo-mechanical coupled computational framework to study diffusion induced large plastic deformation and phase field fracture in Si electrodes. Into this framework we incorporate a recently developed reaction-controlled diffusion model to predict two-phase lithiation for amorphous Si (a-Si) and crystalline Si (c-Si) as well as diffusion induced anisotropic deformation for c-Si. The variational formulation suggests to consider the deformation field, the chemical potential, and the damage field as primary unknowns. The concentration field is considered as a local variable and is recovered from the chemical potential on the element level. We carry out several numerical simulations to show the performance of our computational model and point out the significance of accurately accounting for the presence of the reaction front when modeling diffusion induced fracture problems for both a-Si and c-Si electrodes. In addition, we investigate how the fracture energy release rate, electrode geometry, and geometrical constraints affect the fracture behavior of Si electrodes.

Keywords: Phase-field fracture; Variational principles; Two-phase lithiation; Reaction-controlled diffusion; Silicon electrodes; Lithium-ion batteries

1. Introduction

Lithium-ion batteries are widely used as energy storage devices for portable electronics and electric vehicles [1]. One way to improve their performance is to use new electrode materials. Silicon (Si) is considered to be a promising

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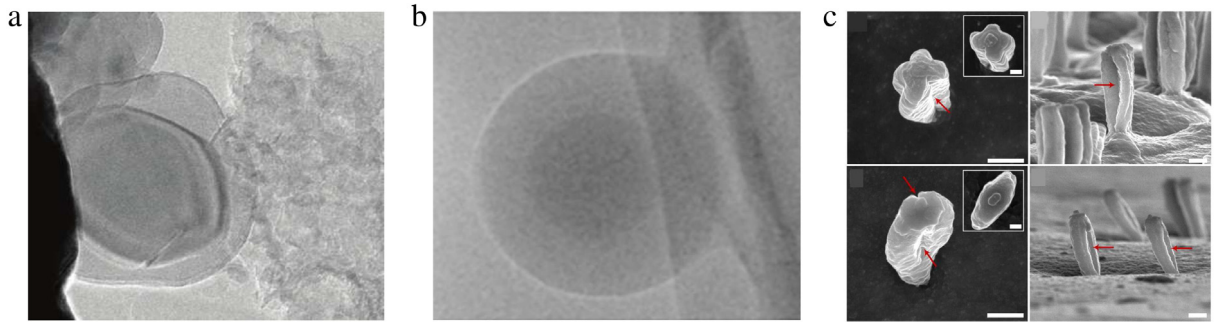

Fig. 1. Illustration of the two-phase lithiation process in Si electrodes for (a) crystalline [3] and (b) amorphous [5] silicon nanoparticles. In both cases a phase boundary is clearly visible. In (c), the diffusion induced anisotropic deformation for crystalline nanopillars [7] is shown.

anode material, characterized by a theoretical specific energy as high as 4200 mAh/g, compared with 372 mAh/g for graphite, the currently most common commercial anode material. However, the large volume change (∼300%) of Si electrodes during (de)lithiation processes leads to high mechanical stresses, mechanical failure, chemical degradation, capacity loss, and therefore currently prevents its practical application.

The Si (de)lithiation process is highly complex, involving mass diffusion, electrochemical reaction, and mechanical deformation. With the development of in situ transmission electron microscopy (TEM) technologies [2], important features involved in the (de)lithiation process of Si have been revealed. As illustrated in Fig. 1, those include two-phase lithiation [3–5] as well as diffusion induced large plastic deformation and fracture [6,7]. During the initial lithiation process, crystalline Si (c-Si) and amorphous Si (a-Si) both undergo two-phase lithiation and are transformed to an amorphous Li_xSi (a-Li_xSi) alloy [3–5]. The two phases (Si and a-Li_xSi) are separated by a sharp reaction front with a thickness of a few nanometers [8,9]. It is interesting to note that the anisotropic volume expansion for c-Si shows a preferred lithiation plane [10,11], while for a-Si, the diffusion induced deformation is isotropic. Fracture phenomena of Si electrodes with different nanostructures are investigated experimentally for both the lithiation [3,7,11,12] and delithiation process [8,13,14], with a strong size dependency during initial lithiation [3]. The fracture energy of lithiated silicon thin-film electrodes is measured in [15] for various Li concentrations. In addition, plastic flow is observed during the (de)lithiation process in thin films, with experimentally measured values for the yield stress provided in [6].

Numerous numerical investigations are carried out in the literature, trying to better understand the experimentally observed complicated mechanical behavior of Si electrodes. Chemo-mechanical coupled models for elasto-plastic deformation at large strain are developed in [16–21] to study the diffusion induced swelling. One can refer to a recent review paper [22] for a more detailed discussion. Theoretical investigations are carried out to study crack nucleation [23,24], the effect of charging rate on the fracture behavior [25,26], the size-dependency of fracture [27], and the resulting anisotropic deformation in c-Si nanopillars [28] during the diffusion process in Si electrodes. To determine the onset of fracture, different crack driving forces are proposed based on a chemo-mechanical coupled J-integral [18], the maximum tensile strength theory [23], or the strain energy release rate [27].

To model the propagation of a crack in a failing material, several numerical tools exist. Successful approaches are the embedded finite element method [29–39] or the extended finite element method [40–43], both describing the crack as a discrete entity. Alternatively, diffusive phase field approaches to fracture [44–48] are currently experiencing a dramatic upsurge as those do not require the geometric information of a possible failure onset and perform well when complicated failure surfaces are expected for cases when multiple cracks are present or when cracks coalesce and branch. The phase field approach to fracture can be traced back to the seminal work of [44,45], where the sharp crack topology is replaced with a regularized crack zone governed by a scalar damage variable and where an elegant variational description of the resulting energy minimization problem is proposed. Extensions are made in [47,49] to account for tension-only induced fracture through a decomposition of the free energy into a tensile and compressive part, and to prevent crack reversal through the introduction of a history field for the crack driving force. A staggered update scheme is proposed in [48,50] to efficiently solve the resulting system of equations. Phase field approaches to brittle fracture are further extended to account for dynamic fracture [51,52], higher order approximations of the damage field [53,54], different types of material [55–58], multiphysics problems [50,59–62], and ductile fracture [63–67].