Phase field modeling of lithium diffusion, finite deformation, stress evolution and crack propagation in lithium ion battery

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HIGHLIGHTS

- A phase field model is built.
- Stress evolutions for silicon particle anode are explored.
- Small deformation and finite deformation model provide different stress states.
- Elastic softening has not a significant effect on stress evolution.
- Plastic flow decreases the magnitude of stress, and changes the stress evolution.

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ABSTRACT

Mechanical degradation under cyclic charging and discharging has been the one of the most important bottlenecks for the developments of lithium ion batteries. Understanding of stress evolution process of anode during cycling is a way to deeply understand the mechanical degradation. In this paper, a phase field model (PFM) coupling lithium diffusion, finite deformation, stress evolution with crack propagation is established. Then the model is applied to spherical silicon particle to explore the stress evolution with taking account of finite deformation, elastic softening and plastic flow. The numerical results show that small deformation model and finite deformation model provide different stress states especially when the anode undergoes a large volumetric expansion. Elastic softening has not a significant effect on stress evolution in spherical particle. Plastic flow decreases the magnitude of stress, and deeply changes the stress evolution, making the hoop stress near the particle surface to become positive during charge process, indicating the particle surface is subjected to tensile hoop stress.

1. Introduction

The rapid developments of electro-equipments, electrical vehicles and high performance computing demand high energy density, high capacity and long service life lithium ion batteries. While traditional carbonaceous materials as the anode material for commercial lithium ion battery cannot meet these requirements [1,2]. Recently, silicon (Si) has

been considered as a more suitable promising anode material than commercial graphite in lithium ion batteries due to it having the highest energy density (4200 mAh g^{-1}) of all other substitutes (e.g., antimony, tin) [3–5]. However, the commercialization of Si anodes is limited by mechanical failure which is the result of the huge volume change (∼400%, due to the fact that each Si atom can theoretically accommodate 4.4 lithium atoms), stress evolution and fracture in charging and discharging cycles [6]. During the electrochemical lithiation process (delithiation process), a large number of lithium ions enter (are extracted from) the Si anode and form a fully charged state

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of $Li_{22}Si_5$ which causes a huge volume change. The resulting large mismatch in volume between the charged region and the non-charged region, combining with constraining by external agencies such as a substrate and current collector tends to induce large stress evolution in the anode. After cycling, these stresses result in damage accumulation, propagation of cracks, even pulverization of particles. As a results, the capacity of the anode drastically fades, and the performance of the batteries starts to degenerate during cycles. In this sense, mechanical degradation under cyclic charging and discharging has been the one of the most important bottlenecks for the developments of lithium ion batteries [6].

There is a great interest in understanding the mechanical degradation of Si anodes for structural reliability during charge and discharge. Consequently, a large body of literature in experiments has appeared in the last decades on diffusion, deformation, stress evolution and fracture in representative battery microstructures. Lithiation of both crystalline Si nanoparticles and amorphous nanoparticles has been studied via in situ transmission electron microscopy (TEM) experiments, which indicates that the first lithiation of the amorphous Si is similar to that of the crystalline Si [7,8]. Colossal volume changes [9] and anomalous shape changes [10] of Si electrodes are also presented in experiments by using in situ atomic force microscopy (AFM) and scanning electron microscopy (SEM). For stress evolution, a number of studies have monitored the stress evolution and property changes in Si thin films by in situ wafer curvature techniques and indentation test during charge and discharge cycles. In these experiments, lithiated Si is found to undergo elastic softening and plastic flow during cycles. An experimental technique with a multi-beam optical sensor to measure the in situ biaxial modulus of a Si thin film electrode as a function of its lithium concentration was reported and it found that the biaxial modulus drops substantially from ca. 70 GPa for $Li_{0.32}Si$ to ca. 35 GPa for $Li_{3.0}Si$ [11]. The ex-situ measurements of the Young's modulus and hardness of Si and Si–Li alloy thin film electrodes at various stages of lithium insertion via depth-sensing indentation experiments indicated that the Young's modulus decrease from an initial value of 92 GPa for pure Si to 12 GPa at full lithium insertion [12]. In addition, nanoindentation testing was used in experiments to determine the Young's modulus of polycrystalline $Li_{22}Si_5$ and the Young's modulus was found to be 35.4 GPa [13]. Such a decrease in Young's modulus is an important manifestation of what is called lithiation-induced softening. Furthermore, a distinct plastic flow stage in stress evolution was reported in the experiments of in situ measurements of stress evolution in a Si thin film electrode during lithiation and delithiation by using the multi-beam optical sensor technique [14]. In addition to studying the stress evolution, much work has been done to study the fracture and crack propagation in Si anodes. Crack evolution in individual Si nanoparticles [15] and Si particles with average sizes of 1–5 μm [16] has been studied with in situ TEM and SEM, respectively. Fracture in Si nanopillars of different axial orientation and size during the first cycle of lithiation and delithiation was investigated and it found that, upon lithiation, fracture sites are located at the surface of nanopillars between neighboring {110} lateral planes [17]. Moreover, cracks in a Si thin film during cycles of lithiation and delithiation were observed [6,18–20]. Recently, the fracture energy of lithiated Si thin film electrodes has been measured and the results have shown that lithiated Si demonstrates a unique ability to flow plastically and fracture in a brittle manner [21].

The abundant experimental results have motivated a large number of model studies of diffusion, stress evolution and fracture in Si anodes. These include detailed models of stress evolution in a particle [22,23], nanowires [24,25] and thin films [26,27]; detailed models of stress induced fracture in an anode [26,28–30]. However, existing models of stress evolution and fracture in battery materials have about three limitations. First, most of the studies restricted the mechanical deformation of Si anodes into infinitesimal deformation. This is a reasonable approximation for a graphitic anode due to the small volumetric strains (∼12%), but is likely to lead to a significant errors for a Si anode which experience large volumetric expansion (∼400%) when fully charged. Some recent studies are notable exceptions which quantified the deformation of the anode by finite deformation model [31–35], but it is still unclear about the difference between small deformation models and finite deformation models. Second, the controlled experimental measurements of elastic properties and stresses in Si thin films during cycles have demonstrated that the Si anode undergoes elastic softening and plastic flow during every cycle. Elastic softening and plastic flow are likely to have a great effect on stress evolution, but the models which deeply explore the effects of elastic softening and plastic flow on stress evolution are still rare in open literature. Third, experiments show that lithium diffusion, stress evolution and crack propagation are three important and coupled processes during charge and discharge. However, nearly most of existing model studies just include lithium diffusion and stress evolution. Recently, a finite element method for modeling deformation, diffusion, and fracture using a cohesive zone has been described, which modeled the fracture during lithiation of thin films [32]. A chemo-mechanical model has been presented to investigate the lithiation-induced phase transformation, morphological evolution, stress generation and fracture in crystalline Si nanowires [35]. These two models give an inspiration in modeling which takes account of lithium diffusion, stress evolution and crack propagation.

The goal in this paper is to address these limitations by using phase field models (PFMs). PFMs, also called diffusion interface models, were introduced for the purpose of avoiding tracking the interfaces. Now, PFMs have emerged as a powerful computational approach to model and predict mesoscale morphological and microstructural evolution in materials [36,37]. Recently, PFMs have been studied in modeling of lithium ion batteries. A PFM has been modeled to assess the conditions under which amorphous phase transitions may occur in nanoscale $LiMPO_4$ [38]. For stress generation in electrode of lithium ion batteries, a PFM coupled to mechanics was presented to demonstrate the relationship between phase segregation and high values of the mechanical stresses in $Li_xMn_2O_4$ [39,40]. A PFM coupled with large elasto-plastic deformation was developed to study the evolution of phase, morphology and