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A multiphysics model that can capture crack patterns in Si thin films based on their microstructure

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HIGHLIGHTS

- Fracture has not been simulated for Si thin films.
- Multiphysics model can capture dry-bed lake fracture.
- Fracture is inhibited for films less than 100 nm.

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ABSTRACT

Fracture in silicon anodes has fascinated the electrochemistry community for two decades, as it can result in a 80% capacity loss over the first few electrochemical cycles and is the limiting factor in commercializing such high capacity anodes. Although numerous experimental data exist illustrating severe fracture patterns and their dependence on the scale of the microstructure, no theoretical model has been able to re-produce and capture such behaviour. In this article, a multi-physics phase-field damage model is presented that can accurately capture the long standing problem of dry bed-lake crack patterns observed for Si thin film anodes. A promising aspect of the model is that, in addition to accounting for Li-ion diffusion, it can explicitly capture the microstructure, and therefore when applied to a Si film with a thickness below 100 nm no fracture was observed, which is consistent with experiments. As fracture in continuous thin films is random, micron-hole patterned Si films were also fabricated and cycled, resulting in ordered crack patterns. The proposed model was able to capture these elaborate, yet ordered, crack patterns, further validating its efficiency in predicting damage during lithiation of Si. This paves the way to using multiscale modeling for predicting the dimensions that limit and control fracture during lithiation, prolonging hence the electrode lifetime.

1. Introduction

Extensive experimental research has concluded that Si-based anodes are the most promising candidates for next generation Li-ion batteries. Upon the formation of Li–Si alloys the theoretical capacity can be as high as 4200mAh/g, which is eleven times higher than that of graphitic anodes (372mAh/g) that are used commercially. The limiting factor, however, in employing Si is that its high capacity cannot be retained due to the volume expansions (up to 400%) that occur upon lithiation and the subsequent fracture that develops. The most prominent example being dry bed-lake fracture that has been observed for Si and SiSn thin film anodes [1,2]. However, it should be noted that microstructure plays a key role in the extent of fracture. Experimental studies have shown that Si films below a critical thickness of 100 nm did not exhibit fracture. This was initially assumed in Ref. [3] since a high capacity retention was obtained for such film thicknesses, but was later proven by performing scanning electron microscopy (SEM) on amorphous Si film anodes that were 100 nm and 500 nm after 10 electrochemical cycles, showing that the 100 nm film remained undamaged while the 500 nm film experienced severe fracture [4]. Similar observations exist for Sn [5] and Si [6] which show that damage is significantly reduced as the particle size decreases.

Although this unique fracture mechanism of dry bed-lake fracture of metal anodes has captured the attention of the mechanics community

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since the early 2000s, a model that can simulate it has yet to be proposed, due to the complexity of the problem. Initial studies used pure mechanical models, without explicitly accounting for Li-ion diffusion, to predict the mechanical stability upon maximum lithiation [7–9]. This allowed for the development of design criteria that predicted the most promising configurations, particle sizes and matrix materials, that would allow for an increased mechanical stability and hence longer anode cycle life. Although the predictions were consistent with experimental observations, the physical mechanisms that drove crack growth during cycling remained unexplored, and therefore subsequent mechanics models incorporated Li-ion diffusion and considered the fully coupled problem of diffusion and deformation. Despite the rigor of these models (a summary of which can be found in Ref. [10]), which employed, for example, generalized finite element models of diffusion, finite deformation, plasticity and fracture within the framework of cohesive zone modeling [11,12], they were not able to capture the dry bed-lake fracture of Si film anodes. More recently phase field modeling has also been used to model damage evolution during the Li-insertion process ([13,14]), however, focus was given mostly on cathodes. When applied to Si film anodes [15] it was not possible to re-produce the experimentally obtained crack patterns.

The purpose of the present work is therefore to propose an experimentally validated multiphysics model that can capture fracture initiation and propagation throughout the continuous Li-insertion and de-insertion process. This is done by using a phase field model which accounts for the mechanical stresses resulting from the volume expansion of Si induced by the Li-ion diffusion. Applying the model to a Si thin film anode allowed to simulate the reknowned dry bed-lake fracture and its dependence on film thickness. To further establish the efficiency of the proposed model it is shown that it can also simulate ordered crack networks that form upon electrochemically cycling a new type of Si thin film that is patterned with micron-holes.

2. Experimental section

2.1. Sample preparation

A *Ti* thin film with a thickness of 500 nm was deposited on a polished quartz substrate by DC magnetron sputtering as the current collector for the electrochemical tests. The pure Si thin films were deposited on the *Ti* /quartz substrate by co-sputtering with pure silicon target (99.999% purity) and pure titanium target (99.5%). The thickness of the silicon film was 650 nm. In the case that the Si film was patterned with periodic arrays of micro-holes, a 1 mm-thick layer of positive photoresist S1813 (Shipley microposit S1813, Massachusetts, USA) was spin coated onto the Si film and pre-baked on a hot plate at 115 °C for 60 s. After 42 s the samples were etched with a 50 nm per min rate by RIE (A PlasmaLab 80 Plus RIE system, Oxford Instruments Company, UK) with methane trifluoride gases. Finally 4.5×4.5 μm micropore array silicon films where the distance between the micropores was 5.50 µm and the depth was 650 nm were obtained as illustrated in the Hitachi S-4800 SEM image Fig. 1(a).

2.2. Electrochemical testing and sample characterization

A Swagelok-type two-electrode cell was assembled in an *Ar* -filled glove box (*MBraun*, H_2O and $O_2 < 0.1$ ppm). The Si film was used as the working electrode, and Li foil was employed as the counter electrode. The electrolyte was 1 mol/L LiPF6 dissolved in ethylene carbonate (EC ≥ 99%): dimethyl carbonate (DMC ≥ 99%) (1:1, v/v). lithium hexafluorophosphate (LiPF6, ≥ 99.99%). The half cell was cycled between 5 mV and 2 V at room temperature using a Land BA2100A battery tester (Wuhan, China). All cells were galvanostatically discharged and charged at a current density of 0.1C. After the 1^{st} discharge (lithiation), 1^{st} charge (delithiation), and 10^{th} charge (delithiation), the cells were disassembled in an *Ar* -filled glove box and sealed in a special vacuum transfer box in order to transfer them to the SEM chamber for morphological studies.

3. Fracture in Si film anodes

3.1. Crack patterns observed experimentally in Si thin films

The scanning electron microscopy images of Fig. 1 depict the two types of Si film anodes considered: (i) continuous Si thin films of 500 nm thickness, (ii) Si films patterned with an array of micro holes. In both cases Ti was used as the current collector and therefore the Si films were deposited on it.

Fig. 1(I) illustrates the change in thickness of the continuous Si film due to Li-ion insertion and Fig. 1(II) the crack network that formed upon the first insertion. Fig. 1(III), (IV) depict the microstructure upon the 1st delithiation, indicating decohesion at the Ti/Si interface. Inducing a hole pattern in the Si film (Fig. 1(a) and (b)) allowed for some accommodation of the volume expansion during Li-insertion as the hole could relieve the accumulated stress the Li-ion diffusion exerted. Upon the maximum 1st lithiation, Fig. 1(c) and (d) illustrate that the hole diameter decreases from 4.5 µm to 3 µm and no failure occurs at the Ti/Si interface. Upon the first delithiation (Fig. 1(e) and (f)), it is seen that an ordered pattern of diagonal cracks connecting the holes is formed. This crack pattern is retained for the first 9 electrochemical cycles as seen in Fig. 1(g) and (h). However, after the tenth delithiation, a new failure network is obtained, which includes a system of disordered secondary cracks as seen in Fig. 1(i), (j), (k), (l). In the sequel a model is developed that can capture failure in both types of these Si anode microstructures.

3.2. Multi-physics model

The multi-physics model elaborated in this paper is based on a phase field damage model [16] coupled with the diffusion equation for Li-ion insertion and de-insertion. Our model exploits the capability of the phase field approach to capture failure in brittle materials. Li-ion insertion/de-insertion produces a volume change in the Si, and the resulting strain is added to the unknown elastic strain to form the total strain derived from the material displacement. Elastic strain is produced through Hooke's classical law for elastic solids, while Fick's law drives the ion-diffusion. Damage evolution is formulated using a variational approach of brittle fracture as suggested in Ref. [16]. A finite element resolution of the coupled problem is adopted for its flexibility to handle arbitrary geometry and boundary conditions.

3.2.1. Ion diffusion

It is assumed that the Li-ion diffusion inside the Si film can be modeled using the standard diffusion equation stating that the rate in Li-ion concentration is proportional to its Laplacian. If c denotes the normalized Li-ion concentration, ranging between 0 and 1, corresponding to full de-insertion and full-insertion, respectively, then the diffusion equation is written using Fick's law as:

$$\frac{\partial c}{\partial t} = D\Delta c \quad (1)$$

In this equation, $\frac{\partial c}{\partial t}$ denotes the rate change in concentration and D the diffusivity parameter. In a fully coupled chemo-mechanical problem, D may depend on the local stress state of the material and a source term proportional to the local stress should also be considered. These terms are not considered herein as they involve material constants that are difficult to measure and because good agreement with the experiments can be obtained even without them, as will be seen in the next section. To account for the saturation in Li-ions during insertion when c reaches 1, a non-linear diffusivity law is adopted. To produce sharp concentration profiles that lead to high stress levels [6], the dependency of D with respect to c is assumed to be: